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Col. = Colorimetric, heterometric, photometric and spectrophotometric analysis — colorimétrie, hétérométrie, photométrie et spectrophotométrie — kolorimetrische, heterometrische, photometrische und spektrophotometrische Analyse
El. = Electrical methods (except polarography) — Méthodes électriques (excepté polarographie) — Elektrische Methoden (ausgenommen Polarographie)
Grav. = Gravimetric and thermogravimetric (*) analysis — Gravimétrie et thermogravimétrie (*) — gravimetrische und thermogravimetrische (*) Analyse
Id. = Identification reactions and qualitative analysis — identification (réactions) et analyse qualitative — Identifizierungsreaktionen und qualitative Analyse
M. = Miscellaneous — divers — Verschiedenes
Pol. = Polarography — polarographie — Polarographie
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Vol. = Volumetric analysis — volumétrie — volumetrische Analyse

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PREMELTING AND THE FORMATION OF SOLID SOLUTIONS

by

A. R. UBBELOHDE

Imperial College of Science and Technology, London (England)

1. INTRODUCTION

As our knowledge grows of the relations between structure and thermodynamic properties of condensed phases, phenomena which were previously obscure or missed find their proper place in chemical physics. Some of the necessary modifications to the classical Phase Rule as applied to solid-solid transformations have recently been discussed in the light of the structural changes taking place[1]. The present paper deals with modifications to the classical Phase Rule as applied to the solid-liquid transformation, and in particular with the phenomena appearing in the solid near the melting point, generally grouped together under the term "premelting"[2].

In the present paper, the term "premelting" refers to changes in properties of the solid as it approaches the melting point, which foreshadow in a lesser degree the changes occurring in the actual transformation from solid to melt. Premelting may include thermodynamic anomalies such as an enhanced specific heat or an enhanced coefficient of thermal expansion as the melting point is approached. It may also include other anomalies, such as enhanced conductance of ionic crystals, or enhanced plasticity.

2. MECHANISMS OF MELTING

As is well known, classical thermodynamics disregards the structure of phases. A transformation from solid to liquid implies a jump between two ***quite independent*** free-energy surfaces, which intersect sharply but more or less accidentally along the transformation curve. On the other hand, structural studies indicate relationships between the solid and melt which are sometimes very close[2]. It is recognised that melts are always more disordered than the solids from which they originate; a measure of the increase of disorder on melting is obtained from the Boltzmann relationship

$$S_f = R \ln W_2/W_1$$

where W_1 and W_2 represent the number of independent ways of realising the arrangements of solid and melt respectively, and S_f is the entropy of fusion. Certain crystal structures are capable of assuming more than one kind of disorder. Each new kind of disorder gives the possibility of a new mechanism of melting, though in many cases solid-liquid transformations involve several mechanisms of melting simultaneously. The most important mechanisms of melting so far discovered (*cf.* reference 2) are:

(*i*) Positional melting, in which the units of structure (atoms or molecules) are randomised with respect to the ideal lattice positions.

(*ii*) Orientational melting, in which mutual orientations of (asymmetric) units of structure are randomised with respect to the ideal lattice at low temperatures. Less common but very important mechanisms of melting include:

(*iii*) Configurational randomisation. This applies to flexible molecules[3] which can assume more than one configuration by "free rotation" about valency bonds. If the difference in energy between different configurations is not large compared with kT, the whole diversity of these configurations will be present in the melt, whereas crystallisation normally selects the configuration that can be packed most economically into the crystal lattice. For the melting of such crystal structures, an increase of configurational entropy is added to the other mechanisms of melting, so that

$$S_f = S_{\text{positional}} + S_{\text{orientl}} + S_{\text{configl}}$$

Examples of this behaviour are well known in organic chemistry, as in the polymethylene series[2] and in many polymer molecules.

Another important effect in certain cases is:

(*iv*) The formation of association complexes in the melt, for example in the melting of certain inorganic salts[4]. In such cases, an increase of entropy due to the formation of a mixture of association complexes contributes a term to the overall entropy so that

$$S_f = S_{\text{positional}} + S_{\text{orientl}} + S_{\text{assocn}}$$

3. PREMELTING

The present paper does not aim to detail peculiarities of these and of other structural changes that accompany increases of entropy ***in the actual melting process***. The following comments refer to their bearing on premelting phenomena. Premelting can be described as a universal phenomenon, but it is far from being equally prominent in different crystal structures.

The various kinds of disorder which are found in mechanisms of melting are associated with increases of energy U of each unit of structure, relative to the ideal crystal lattice: $U_{\text{positional}}$, $U_{\text{orientational}}$, $U_{\text{configurational}}$ and so on. A corresponding fraction of lattice defects of the order $\frac{n}{N} = \exp(-U/kT)$ will already be present in the crystals below the melting point, in accordance with standard theory. In this sense, all solids must exhibit premelting phenomena, since they all contain a calculable proportion of the same kind of defect of order, as occurs in a bigger proportion on melting. Nevertheless, melting is not a gradual or continuous process. Except above possible critical melting temperatures and pressures[5] melting involves discontinuous changes in specific volume and in heat content, on passing from the solid to the liquid phase. This arises essentially because for the various kinds of disorder U decreases as the fraction of disordered units increases. Such a co-operative decrease permits the co-existence of two condensed phases with different degrees of order and different heat contents, but the same free energies, at the melting point.

All solids exhibit premelting, but only a small number of crystal structures exhibit premelting to any marked degree. One requirement is that the crystal structure must be capable of undergoing extensive disorder, involving values of U/k comparatively small relative to T_f.

For example, in ionic crystal lattices marked premelting phenomena are observed for lithium salts such as LiF and in silver salts such as AgBr (see the literature cited in reference 1). This is probably because in such salts the small strongly polarising cations can occupy positions other than at the ideal lattice points, without involving large values of U/k. For the other alkali halides, the value of U/k can only be lowered sufficiently to give appreciable defect formation by co-operative expansion of the whole assembly. This has to await the onset of melting, which necessarily involves a large increase in specific volume[6]. So far as is known, the other alkali halides do not exhibit premelting to an extent comparable with lithium or silver salts, though further experimentation seems desirable to test this point.

Again in crystals of organic compounds where the lattice forces are of the van der Waals types orientational randomisation of the molecules can be achieved with values of U/k comparatively small relative to T_f, in those cases where the repulsion envelopes of the molecules are already nearly spherical or cylindrical.

For example, in crystalline benzene various structural evidence (nuclear magnetic resonance studies[7], infra-red and Raman studies[8], X-ray intensity measurements[9], compressibility measurements[10]) indicates that the molecules begin to randomise orientation about their hexad axes just below the melting point, so that extensive orientational premelting becomes possible.

The marked premelting observed in alkali metals such as Na or K (see the literature cited in reference 1) is probably due to the fact that positional randomisation need not involve large repulsion forces so that U/k remains small for positional randomisation. Evidence that a close packed arrangement of atoms has practically the same free energy as the bcc arrangement found for alkali metals under ordinary conditions has been obtained from studies on the mechanical deformation of alkali metals. Other examples of marked premelting must be linked with similar and other structural possibilities in the crystals for increasing disorder without the expenditure of much energy.

4. "HETEROPHASE FLUCTUATIONS"

Brief mention may be made of the concept of "heterophase fluctuations" introduced by FRENKEL[11] to account for premelting phenomena. It is important to avoid mere thermodynamic generalities in describing such fluctuations, and to arrive at clear views about their structure. This is not done adequately by FRENKEL.

Even if his theory is mathematically consistent it lacks structural precision, except possibly for the simplest types of crystal structure which in fact may not show extensive premelting. Defect sites in a crystal can involve Schottky or Frenkel positional disorder, or orientational disorder for non-spherical units of structure, or chemical disorder[12], or other types of departure from the ideal crystal lattice. So long as such defect sites are isolated from one another, so that their energies of formation are independent of neighbouring defect sites, it seems quite unwarranted to describe them as "heterophase fluctuations" even though strictly speaking they lead to premelting. However, when neighbouring defect sites are formed in a solid, in various

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kinds of "*co-operative* defects"[13], there are certain resemblances with micro-regions of "liquid" in the crystal lattice. Even so, FRENKEL's nomenclature seems inappropriate for structural reasons even if thermodynamically acceptable.

5. CRITERIA FOR PREMELTING

The range of techniques available for investigating premelting phenomena has increased considerably within recent years. It is always highly desirable to include structural studies as well as thermodynamic measurements when investigating premelting. By themselves, thermodynamic anomalies in properties such as the specific heat or co-efficient of expansion always raise the doubt that they may have a trivial origin. If the sample of material under investigation contains a mole fraction n/N of impurity *soluble in the liquid but not in the solid phase*, the presence of such impurity produces small quantities of solution below the ideal freezing point T_f of the pure substance. Due to the presence of this solution as a fraction $(1-x)$ of the whole, at temperature T_x any thermodynamic property P_r in fact refers to a composite of x of solid and $(1-x)$ of solution. If $\triangle P_r^\circ$ refers to the total change of the observed property on passing from 100% solid to 100% melt, and if the impurity is assumed to obey Raoult's law with freezing point depression constant K it can readily be shown that

$$\triangle P_r^\circ/\triangle P_r = 1/(1-x) = (T_f - T_x)/(nK/N)$$

Plots of $1/\triangle P_r$ against T_x should give a straight line if this trivial explanation accounts for the anomalies observed. Various instances are known where this thermodynamic criterion can be used to eliminate the trivial explanation and to establish homophase premelting, because the impurities in fact form solid solutions[2a,2c] or because their amount and behaviour in heterophase premelting would be quite unlikely[14]. Even in such cases, however, structural studies on the solids near their melting points give precious additional information on premelting. For example, premelting in the paraffins appears to be associated with orientational randomisation about the long chain axes of the molecules (*cf.* the literature cited in reference 1). Again, in ionic crystals, if premelting is due to homophase positional defects, the same activation energy should be calculated from measurements of thermodynamic properties P_r and plots of $\log \triangle P_r$ against $1/T$, as is inferred from structural measurements and plots, for example, of $\log \sigma$ against $1/T$ where σ is the ionic conductance. Tests made so far on this basis for silver salts and alkali thiocyanates show reasonable though not complete concordance between thermodynamic and structural measurements on premelting, as might be expected if more than one defect type is being formed in the solid just below the melting point[14].

6. PREMELTING AND THE FORMATION OF SOLID SOLUTIONS

The behaviour of solid solutions is of particular interest in relation to phenomena of premelting. According to classical theory, when solid solutions are formed, freezing point depressions $\triangle T$ can be related to the mole fraction N_2 of the solute in terms of the distribution coefficient k of solute between melt and solid. The Van 't Hoff equation is[15]

$$\mathrm{d}T/\mathrm{d}N_2 = (k-1)\ RT_f{}^2/(\overline{H}_1 - \overline{H}_1{}')$$

where T_f is the freezing point, H_1 the partial molal heat content of the solvent in the liquid phase, and H_1' the partial molal heat content of the solid in the solid phase.

A case of particular interest for the present discussion is where solute and solvent molecules have rather similar structures, so that the impurity is extremely difficult to get rid of. In such a case, the partial molal heat content H_1 of the solvent in the melt can usually be replaced by the molal heat content of the pure solvent as melt, H_1. When k is small compared with unity, so that not much solid solution in fact takes place, H_1' can also be replaced, though with rather less accuracy, by the molal heat content of the pure solvent as solid, H_1'. The Raoult-Van 't Hoff freezing point equation then takes the form

$$\mathrm{d}T/\mathrm{d}N_2 = (k-1)\ RT_f^2/(H_1 - H_1') = (k-1)\ RT_f^2/H_f$$

where the heat of fusion is

$$H_f = H_1 - H_1'$$

This modification is comparatively trivial.

However, when solute and solvent molecules are very closely similar, as happens particularly in many organic substances which are exceptionally hard to free from related impurities, the values of k can become comparable with unity. At low values of N_2 the assumption $H_1 \sim H_1$ still applies in solution. But in the more highly ordered crystal, more extensive solid solution of closely related impurities can seriously modify crystal repulsion forces which in turn control the proportion of defects in premelting. The extreme is a paradox. In the upper limit, for $k = 1$, the classical equation gives no change at all of freezing point due to even extensive solid solution. In fact, however, the modified crystal forces in the solid solution lead to marked changes of freezing point, due to changes in the values of U/k for various types of defect operative in the mechanisms of melting that apply to the crystals under discussion. Melting points of organic substances are sometimes wrongly interpreted through neglect of these considerations. For example, the melting points of certain polymethylene hydrocarbons are actually raised by impurities of molecules whose structure is so closely related that $k \sim 1$ (*cf.* the literature cited in reference 13). In such cases, a choice between rival preparations should not necessarily give the preference to the sample with highest melting point. Other structural studies are essential when thermodynamic criteria break down, as in the case quoted. Another effect of solid solution can be to modify the onset of randomisation of orientation of unsymmetrical molecules in crystals. This effect is well known in solid-solid transformations, for example in methane/krypton mixtures[16]. In the premelting region, a corresponding effect has been suggested for benzene containing closely related molecules such as thiophene[17]. In many systems of more complex structure, solid solution is likewise difficult to avoid, because of the closely related molecular structures of solvent and solute. The discussion presented here suggests that melting phenomena may be far from straightforward in such cases.

SUMMARY

Possibilities for the occurrence of marked premelting are reviewed for various types of crystal lattice. Examination of criteria for the detection of homophase premelting involves careful consideration of the effects of forming solid solutions, when impurities are present. Some of the consequences of forming solid solutions are discussed in relation to premelting phenomena.

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RÉSUMÉ

L'auteur considère, pour plusieurs types des réseaux oristallins les possibilités d'occurrence d'un phénomène de ,,premelting'' (préfusion) marqué. Par ,,premelting'' il entend tous les changements de propriétés du corps solide à l'approche du point de fusion. Lorsqu'on examine les critères d'un ,,premelting'' homophasé il faut bien tenir compte des effets de formation de solutions solides, dans le cas ou des impuretés sont présentes. Quelques conséquences de la formation de solutions solides sont discutées en relation avec les phénomènes de ,,premelting''.

ZUSAMMENFASSUNG

Der Verfasser gibt eine Übersicht über die Möglichkeiten des Auftretens eines bedeutenden ,,premelting'' für verschiedene Typen von Kristallgittern. Unter ,,premelting'' werden in dieser Arbeit alle Änderungen der Eigenschaften des festen Stoffes wenn er sich dem Schmelzpunkt nähert, verstanden. Wenn man die Kriterien des Nachweises eines homophasischen ,,premelting'' prüft, muss man den Auswirkungen der Bildung fester Lösungen für den Fall dass Verunreinigungen anwesend sind, sorgfältig Rechnung tragen. Einige Folgen der Bildung von festen Lösungen werden im Zusammenhang mit ,,premelting''-Erscheinungen erörtert.

REFERENCES

[1] A. R. Ubbelohde, *Brit. J. Appl. Phys.*, 7 (1956) 313; *Quart. Revs. (London)*, 11 (1957).
[2] (a) A. R. Ubbelohde, *Trans. Faraday Soc.*, 34 (1938) 289.
(b) A. R. Ubbelohde, *Ann. Repts. on Progress Chem.*, 37 (1940) 167.
(c) A. R. Ubbelohde, *Quart. Revs. (London)*, 4 (1950) 356.
[3] J. C. McCoubrey and A. R. Ubbelohde, *Quart. Revs. (London)*, 5 (1951) 364.
[4] W. J. Davis, S. E. Rogers and A. R. Ubbelohde, *Proc. Roy. Soc. London*, 220A (1953) 14.
[5] L. Ebert, *Österr. Chem. Ztg.*, 55 (1954) 1; cf. also the literature cited in reference 1.
[6] G. Landon and A. R. Ubbelohde, *Trans. Faraday Soc.*, 52 (1956) 647; E. Vogel, H. Schinke and F. Sauerwald, *Z. anorg. Chem.*, 284 (1956) 131.
[7] E. R. Andrew and R. G. Eades, *Proc. Roy. Soc. London*, 218A (1953) 537.
[8] A. Frühling, *Ann. phys.*, 6 (1951) 401.
[9] G. S. Parry, private communication.
[10] L. A. K. Staveley and D. N. Parham, *Compt. rend. réunion ann. avec comm. thermodynam Union intern. phys. (Paris)*, 1952. Changements de phases, p. 366.
[11] J. Frenkel, *Kinetic Theory of Liquids*, Oxford University Press, London, 1946.
[12] A. R. Ubbelohde and K. J. Gallagher, *Acta Cryst.*, 8 (1955) 1.
[13] J. W. H. Oldham and A. R. Ubbelohde, *Proc. Roy. Soc. London*, 176A (1940) 50.
[14] D. Plester, S. E. Rogers and A. R. Ubbelohde, *Proc. Roy. Soc. London*, 235A (1956) 469.
[15] G. N. A. Lewis and M. Randall, *Thermodynamics*, McGraw-Hill Book Comp., New York, 1923, Chapter XX, equation (19); see also reference 13.
[16] A. Eucken and H. Veith, *Z. physik. Chem.*, 38B (1938) 393.
[17] F. W. Thompson and A. R. Ubbelohde, *Trans. Faraday Soc.*, 46 (1950) 349.

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MOLECULAR ROTATION AND TRANSLATION IN CRYSTALS OF COMPOUNDS FORMED BETWEEN HIGHLY BRANCHED HYDROCARBONS*

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1. INTRODUCTION

Highly branched hydrocarbons belong to the class of compounds which TIMMERMANS classed as *molecules globulaires*[1]. TIMMERMANS pointed out that the flow of crystalline cyclohexane (a *molecule globulaire*) occurs through a 1 mm capillary at somewhat less than half the pressure required for crystalline *p*-dichlorobenzene and suggested that this is due to some freedom of translation in the crystal.

Compounds which can be classed as *molecules globulaires* usually form solid solutions with each other making separation from each other by fractional crystallization practically impossible. Since the branched hydrocarbons are of such general interest, the behavior of the pure solids and the solid solutions, down to temperatures considerably below the melting point, with respect to the number and nature of transitions in the solid state is of special interest.

2. EVIDENCE FOR ROTATION

By means of studies of the narrowing of the nuclear magnetic absorption line, it has been shown that methane[2,3] and highly branched organic compounds[4] rotate in the solid state. Except in the case of methane, the initial narrowing in the nuclear magnetic resonance line occurs at a transition which is believed to be a rotational transition.

3. EVIDENCE FOR MIGRATION

These rotational transitions have a latent heat several times that of fusion. In compounds where they occur, the entropy of fusion is frequently less than the communal entropy for a liquid (R) accompanying fusion of a monatomic solid[5]. A lower entropy of fusion than that corresponding to the communal entropy of a liquid indicates communal entropy due to freedom of migration in the rotating crystal. Such freedom to migrate has already been suggested by RUSHWORTH for cyclopentane above the rotational transition[6], on the basis that in the rotating solid below the melting point the nuclear resonance line is only 0.03 gauss compared to a value of 1.72 gauss calculated on the basis of rotation alone.

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4. SOLID SOLUTION AND COMPOUND FORMATION

It has been shown that hydrocarbons which rotate in the solid state form solid solutions. These solid solutions frequently have maxima indicating compound formation accompanied by the characteristic eutectics accompanying such compound formation. An example of such a system is shown in Fig. 2 which is the solid liquid equilibrium diagram for the system cyclopentane-2,2-dimethylbutane.

5. BEHAVIOR OF SUPERCOOLED SOLID SOLUTIONS

The investigation of the continuous system of solid solutions formed between 2,2-dimethylbutane and 2,3-dimethylbutane has proved particularly interesting. In the original investigation of this system[7] heat capacity determinations down to low temperatures were made in order to detect phase changes. The author would like to emphasize that even relatively rough heat capacity determinations are more sensitive than a study of cooling rates and are just as convenient compared to cooling rate studies when the latter are made with the proper precautions.

There is a compound D_2N_3 where D and N respectively represent one mole of 2,3-dimethylbutane (diisopropyl) and one mole of 2,2-dimethylbutane (neohexane). No evidence of a rotational transition was found in any of the mixtures. A nuclear magnetic resonance study[8] clearly showed a sharp line narrowing from about 3.0 to 0.3 gauss on fusion in all of the mixtures. On cooling to 20°K, in the region 64°K to 85°K, all mixtures showed a broadening of the line from 3.2 to 8.3 gauss which was not associated with any transition. There was no transition apparent from rough heat capacity measurements at any temperature below that at which definite melting occurred.

Thus a careful investigation was made of the heat capacity from 12°K to room temperature of the mixture D_2N_3 in which compound formation occurred.

Fig. 1 is a graph of the heat capacity against the temperature. Superimposed on this is a graph of the width of the nuclear resonance line in gauss against temperature in the region where the marked broadening occurred on cooling. It is quite evident that this broadening is to be correlated with the almost vertical fall of the heat

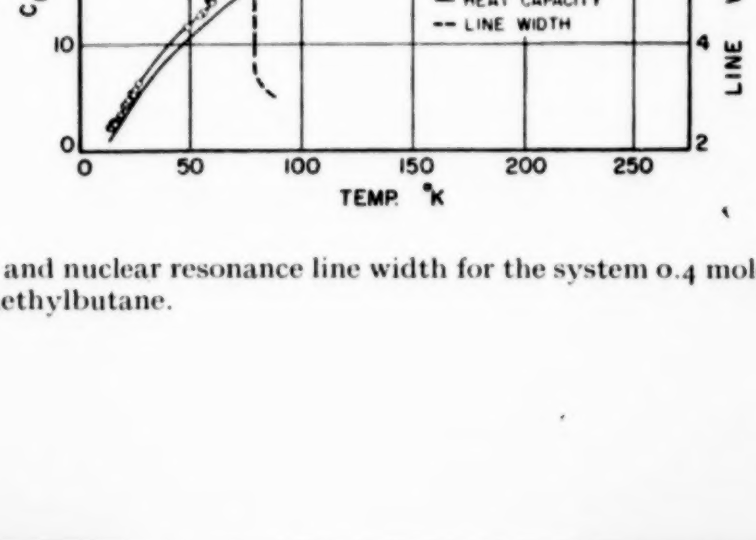

Fig. 1. Heat capacity and nuclear resonance line width for the system 0.4 mole 2,3-dimethylbutane and 0.6 mole 2,2-dimethylbutane.

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capacity curve at about 70°K. There is a definite peak in the heat capacity curve preceding this fall, and the curve is typical of that for an organic glass such as glycerol[9a] and butene-1[9b].

It should be noted carefully that these heat capacity effects are not in a liquid but in a crystalline solid. The temperature of melting of this solid is marked on the graph. The latest heat of fusion is 274 cal mole^{-1}. There seems no way to account for the heat capacity curve other than by postulating that the rotating solid, instead of undergoing the rotational transition, supercools and undergoes a change entirely analogous to vitrification. Such a phenomenon would only be possible if there were migration as well as rotation in the crystal.

On the assumption that the entropy of the liquid could be calculated by taking the sum of the entropies of the components and the entropy of mixing ($-0.6\,R \ln 0.6 - 0.4\,R \ln 0.4 = 1.34$ cal deg^{-1} mole^{-1}), it was possible to calculate the entropy of this glass at the absolute zero using the third law of thermodynamics. If there were no entropy at the absolute zero, the entropy of the liquid should be equal to the change in entropy in going from the absolute zero to the liquid state.

The entropy at 0°K turned out to be 2.40 cal deg^{-1} for one mole of mixture. Subtracting from this the entropy of mixing leaves 1.06 cal deg^{-1} mole^{-1} due to frozen in communal entropy and rotational disorder. From the entropy of fusion (1.61 cal deg^{-1} mole^{-1}) it could be estimated that the communal entropy in the solid was about 0.4 cal deg^{-1} mole^{-1}.

6. ROTATIONAL TRANSITIONS IN SOLID SOLUTIONS

In the system studied in the last paragraph, supercooling prevented a study of rotational transitions in the solid solution. In the system cyclopentane-2,2-dimethylbutane[7] supercooling does not occur, and a rotational transition can be observed both in heat capacity determinations and in the nuclear magnetic resonance studies. For convenience the boiling points, triple points, and temperatures of the upper and lower transitions are listed in Table I. In both cases the α, β and γ respectively denote the non-rotating form, the rotating form stable at the low temperature and the rotating form stable immediately below the melting point. It will be noticed that not only are there the same number of transitions, but the temperatures of the corresponding phase changes are surprisingly close. The fact that the boiling points differ only by 0.5° turns out to be very convenient for the necessary entropy of vaporization measurements.

TABLE I

BOILING, TRIPLE, AND TRANSITION POINTS OF CYCLOPENTANE (C) AND 2,2-DIMETHYLBUTANE (N)

	Compound	
	C (°K)	*N (°K)*
Boiling point (724.5 mm)	320.99	321.50
Melting point	179.70	174.16
Transition $\beta \rightarrow \gamma$	138.07	140.88
Transition $\alpha \rightarrow \beta$	122.39	126.81

The temperatures of solid-liquid equilibrium and of the α to β transitions are plotted against composition in Fig. 2. Curve D represents the temperatures of the α to β transition. The temperatures of the β to γ transitions are not included because this was obscured by melting in many cases.

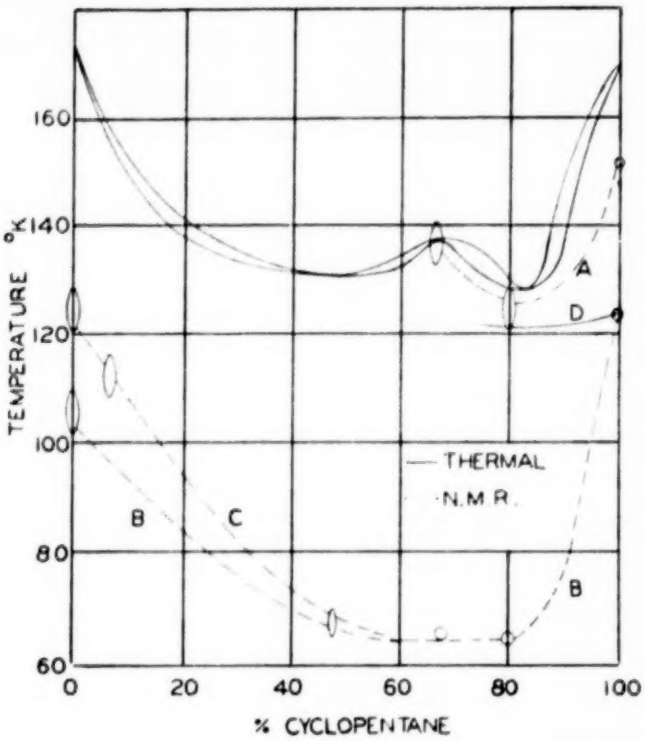

Fig. 2. Solid-liquid equilibrium and lower transition temperatures for the system cyclopentane and 2,2-dimethylbutane.

Inspection of the graph shows that there is little change in the temperature of the α to β transition with composition. However, below 73.6 mole per cent cyclopentane, the heat effect was so small that the transition could not be detected[7]. A graph of the heats of transition against mole per cent cyclopentane in the solid solution was a straight line which extrapolated to zero heat in the neighborhood of 70 mole per cent cyclopentane. In keeping with this there was no α to β transition in the mixture containing 70.1 mole per cent cyclopentane. In Fig. 2 the dotted lines represent the temperatures of marked change in line width (narrowing on heating). Curves B, C, and A are, respectively, for changes of 20 to 9.0 gauss, 9 to 2.5 gauss, and 2.5 to 1 gauss.

The conclusion to be drawn from these facts is that only cyclopentane in excess of 70 mole per cent participates in the rotational transition, leaving the remainder in the rotating state either as complex or solid solutions in the complex*. Heats calculated assuming that only this excess partakes in the transition are all equal to the heat of the transition in pure cyclopentane.

A careful set of heat capacities has been taken from 14°K to room temperature in the mixture which contains 69.3 mole per cent cyclopentane. In this there was no sign of the α to β rotational transition, but there was a second order rotational transition with its maximum at 83.15°K, and the low temperature side extending to 70°K. It will later be shown that at the maximum temperature of this transition the complex separates from solid solutions of cyclopentane in the complex as the latter loses its rotational freedom and finally the solid solution, now richer in cyclopentane, loses its ability to rotate.

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* In reference 7 it was thought that only the cyclopentane in excess of 66.6 mole per cent could partake in the transition. The data can be better explained by increasing this value to 70 mole per cent.

A careful set of heat capacities down to 14°K taken in the mixture containing 66.7 mole per cent cyclopentane (NC_2) also showed the second order rotational transition with a maximum at 83.2°K and extending to about 70°K on the low temperature side.

Fig. 3 is a graph of these heat capacities against temperature. The dotted curve represents nuclear resonance line width. The first decrease in line width from 12 to 2.5 gauss occurs on heating to about 65°K which is just below the temperature at which the second order transition is first apparent. A further decrease to below 1 gauss occurs at the melting point.

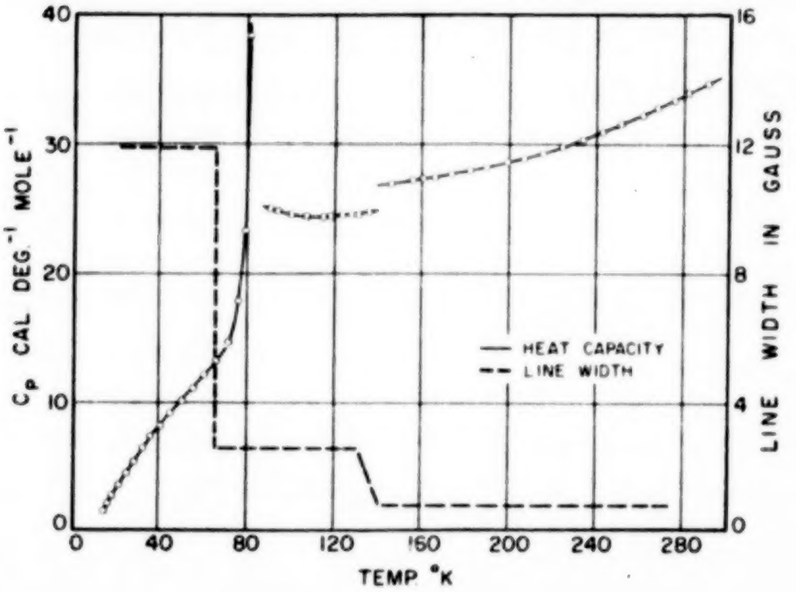

Fig. 3. Heat capacity and nuclear resonance data for the system 0.333 mole 2,2-dimethylbutane and 0.667 mole cyclopentane.

In the case of the formation of the "*rotational glass*" in the system 2,2-dimethylbutane and 2,3-dimethylbutane there is a corresponding line narrowing in the region of sharp rise of heat capacity at 70°K.

For most substances the sharp fall in heat capacity connected with vitrification occurs on supercooling not far below the melting point. It might thus be guessed that in this system there would be a rotational transition at about 70°K if there were not supercooling.

7. THE ENTROPY OF THE SOLID SOLUTION OF COMPOSITION NC_2 AT 0°K

In addition to the heat capacity measurements down to 14°K recorded in Fig. 3, heats of transition, fusion, and vaporization at 298.16°K, as well as vapor pressures, were taken on the solid solutions of the two compositions mentioned in the last section. In the case of the solid solution of composition NC_2, the data made it possible to calculate the increase in entropy in going from 0°K to the ideal gas state at 298.16°K and one atmosphere. This value could then be compared with the value of the entropy of the ideally gaseous mixture calculated from the entropies of the components[10 11] plus an entropy of mixing of

$$S_{\text{mix}} = -R(0.333 \ln 0.333 + 0.667 \ln 0.667) = 1.27 \text{ cal deg}^{-1} \text{ mole}^{-1} \quad . \; . \; . \; . \; . \; . \quad (1)$$

To obtain the entropy of vaporization, a careful study of the vapor pressures of mixtures of cyclopentane and 2,2-dimethylbutane was made. At 306.5°K the vapor pressures ranged from 439.5 to 441 mm over the entire range of composition. At a pressure of one atmosphere, the boiling point curve had a flat minimum over the range from 55 mole per cent to 90 mole per cent cyclopentane which was about 0.1° below the boiling point of cyclopentane. Over this range the boiling point varied only 0.08°. Thus the 66.6 mole per cent and the 69 mole per cent cyclopentane mixtures could be considered as pure compounds while measuring the heats of vaporization and the vapor pressure temperature relationships.

Table II summarizes the calculation of the entropy of the 66.6 mole per cent cyclopentane mixture at the absolute zero from all of the data. The value is 1.12 ± 0.2 cal deg^{-1} mole^{-1}. This must be multiplied by three to obtain the value for one unit of the compound NC_2. The value, 3.36, thus obtained is within experimental error of R ln 5 (equal to 3.20 cal deg^{-1} mole^{-1}). This could be interpreted as due to five possible orientations of the compound. Due to the fact that the transition is second order and has replaced two pairs of transitions for the components, it is hard to see that the cyclopentane and 2,2-dimethylbutane molecules could be other than arranged in groups, each consisting of a pair of cyclopentane molecules with a 2,2-dimethylbutane molecule. That the 1.12 cal deg^{-1} mole^{-1} could be an entropy of mixing is thus unlikely in spite of the fact that the value is close to the entropy of mixing per mole as given by equation (1) (1.27).

TABLE II

THE ENTROPY OF THE GASEOUS 0.66602 MOLE CYCLOPENTANE, 0.33398 MOLE 2,2-DIMETHYLBUTANE MIXTURE AT 298.16°K

Contribution	*ΔS cal deg^{-1} mole^{-1}*
0-15°K, Debye function, $\Theta = 108$ (5 degrees of freedom)	0.653 ± 0.02
15°K-83.200°K (graphical $\int C_p/T\, dT$)	13.453 ± 0.04
Second order transition	4.014 ± 0.01
83.200°K-137.710°K (graphical $\int C_p/T\, dT$)	12.476 ± 0.00
Fusion 200.27/137.71	1.454 ± 0.01
137.710°K-298.160°K (graphical $\int C_p/T\, dT$)	22.891 ± 0.02
Entropy of the liquid at 298.16°K =	54.941 ± 0.10 e.u.
Vaporization at 298.16°K (6722/298.16)	22.54 ± 0.06
Gas imperfection correction	0.09
Correction to 1 atmosphere	—1.70
$S - S_0$ of the ideal gas at 1 atm, 298.16°K =	75.87 ± 0.16
Absolute entropy of ideal gas calculated from components (less nuclear spin)	76.99 ± 0.10
Entropy at 0°K (S_0)	1.12 ± 0.2

8. THE ENTROPY OF THE MIXTURE CONTAINING 69 MOLE PER CENT OF CYCLOPENTANE

Using the same procedure as in the last paragraph, the entropy per gram mole of mixture at the absolute zero was found to be 0.91 cal deg^{-1} per mole of mixture, whereas the entropy of mixing should be 1.23 cal deg^{-1} mole^{-1}.

In one mole of the 69 mole per cent mixture, there is only 0.920 moles* of the compound NC_2. If the cyclopentane has phase separated, the entropy of mixing in the solid solution of composition NC_2, present in one mole, would still be 1.27 times 0.920, or 1.17 cal deg^{-1} which is higher than the experimental value by the full experimental error. However, the zero point entropy per mole of mixture, if the complex had an entropy of $R \ln 5$ per NC_2 unit, would be

$$S_0 = 3.20 \times 0.920/3 = 0.98 \text{ cal deg}^{-1} \qquad (2)$$

This value is very close to the experimentally found value. While the agreement has involved amounts which are barely within the experimental error, the heat capacity curves do show that at or below the rotational transition 0.6 cal deg^{-1} more entropy is removed per mole from the 69 mole per cent cyclopentane mixture than that calculated on the basis of that for the compound NC_2, assuming no excess cyclopentane contribution. Combining this with the difference in entropy from that calculated up to the transition which is 0.20 cal deg^{-1} mole^{-1}, the excess removed is 0.8 cal deg^{-1} mole^{-1}. The entropy of mixing of the cyclopentane with the compound NC_2 is 0.39 cal deg^{-1}. The difference between the two figures must be due to rotational entropy removed from the cyclopentane.

9. FINAL REMARKS

It has already been remarked[8] that in highly branched molecules which do not have tetrahedral symmetry, rotational transitions are first order. When the molecules have tetrahedral symmetry the transitions are second order. This is probably due to the fact that in the less symmetrical molecules there is cooperation between rotation and translational migration. The second order transition in the compound NC_2 could thus be due to its high symmetry.

SUMMARY

Highly branched hydrocarbons rotate in the solid state and form solid solutions with compound formation. The compounds have a characteristic rotational transition replacing entirely the first order rotational transition of the components. The rotating crystalline solid solutions with the composition of the compound can be supercooled. The supercooled rotating solid behaves exactly like a glass. Certain deductions are made from these facts.

RÉSUMÉ

Les hydrocarbures fortement ramifiés montrent une rotation à l'état solide et donnent des solutions solides avec formation de composés. Les composés ont une transition rotatoire caractéristique remplaçant totalement la transition rotatoire du premier ordre des composantes. Les solutions solides cristallines douées de rotation et qui ont la composition d'un composé peuvent être portées à l'état de surfusion. Le solide à l'état de surfusion se comporte exactement comme un verre. L'auteur fait certaines déductions de ces faits.

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[*] The mole equals $NC_2/3$.

ZUSAMMENFASSUNG

Hochverzweigte Kohlenwasserstoffe rotieren im festen Zustand und bilden feste Lösungen unter Bildung von Verbindungen. Die Verbindungen haben einen charakteristischen Rotationsübergang welcher den Rotationsübergang erster Ordnung der Komponenten vollständig ersetzt. Die rotierenden festen Lösungen deren Zusammensetzung einer Verbindung entspricht können unterkühlt werden. Der unterkühlte rotierende feste Stoff verhält sich genau wie ein Glas. Aus diesen Tatsachen werden gewisse Folgerungen abgeleitet.

REFERENCES

[1] J. Timmermans, *J. Chem. Phys.*, 35 (1938) 332.
[2] F. Bitter, N. L. Alpert, H. L. Poss, C. G. Lehr and S. T. Lin, *Phys. Rev.*, 71 (1947) 738.
[3] N. L. Alpert, *Phys. Rev.*, 72 (1947) 637.
[4] H. S. Gutowsky and G. E. Pahe, *J. Chem. Phys.*, 18 (1950) 162.
[5] J. G. Aston, H. L. Fink and S. C. Schumann, *J. Am. Chem. Soc.*, 65 (1943) 341.
[6] F. A. Rushworth, *Proc. Roy. Soc. London A*, 222 (1954) 526.
[7] H. L. Fink, M. R. Cines, F. E. Fry and J. G. Aston, *J. Am. Chem. Soc.*, 69 (1947) 1501.
[8] J. G. Aston, H. Segall and N. Fuschillo, *J. Chem. Phys.*, 24 (1956) 1061.
[9a] G. E. Gibson and W. F. Giauque, *J. Am. Chem. Soc.*, 45 (1923) 93.
[9b] J. G. Aston, H. L. Fink, A. B. Bestful, E. L. Pace and G. J. Szasz, *J. Am. Chem. Soc.*, 68 (1946) 52.
[10] J. G. Aston, H. L. Fink and S. C. Schumann, *J. Am. Chem. Soc.*, 65 (1943) 341.
[11] J. E. Kilpatrick and K. S. Pitzer, *J. Am. Chem. Soc.*, 68 (1947) 1066.

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SOME CONSIDERATIONS GOVERNING THE CHOICE OF METHOD FOR PURITY DETERMINATIONS BY CRYOSCOPY

by

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1. INTRODUCTION

The use of the cryoscopic behaviour of a material for the determination of its purity is now a well established technique and no attempt will be made to present an exhaustive review of existent procedures. This paper is concerned with some of the factors which govern the choice of the experimental conditions when dynamic methods are employed. Static methods for studying the solid-liquid systems will not be considered because they are not widely employed for assessing purity probably because the apparatus is difficult to construct and because much subsidiary equipment is required.

The discussion will be restricted to systems in which the impurity is soluble in the liquid but insoluble in the main solid phase because it is only for such systems that the moles per cent impurity can be determined without a detailed knowledge of the chemical nature of the impurity[1]. Further, the considerations will be confined to those systems where the 100% pure material is believed to melt completely at a single temperature and a discussion of substances such as polyethylene which contain amorphous and crystalline regions in the solid will be excluded.

2. FREEZING CURVES

The concentration of impurity in a sample is often determined by the study of the shape of freezing curves such as those shown in Fig. 1. In such curves the stationary temperature reached after seeding a 100% pure material does not equal the true melting point because the system is a dynamic one[2]. The rate of melting and the rate of freezing are equal when thermodynamic equilibrium is achieved but if the amount frozen is increasing as it is in the experiments the results of which are depicted in Fig. 1 then the stationary temperature must be below the thermodynamic equilibrium temperature.

An estimation of the difference in temperature between the stationary and true equilibrium value is difficult but it is known that the rate of crystallization of organic materials may be low. For example TIMMERMANS[3] quotes the following values for the "vitesse de cristallisation": *o*-cresol, rate 294 mm/min when supercooled 30°C; *m*-cresol, rate 240 mm/min when supercooled 26°C; and *p*-cresol, rate 240 mm/min when supercooled 26°C. Consideration of these figures using a modification of an argument employed by CHALMERS[4] suggests that the difference between the equilibrium and stationary temperatures for *m*-cresol might amount to several hundredths of a degree Celsius even if the liquid is well stirred and growth is taking place simultaneously from several crystals. A similar conclusion is reached if the theory of crystal growth discussed by HULLIG AND TURNBULL[5] is employed. To keep the temperature difference between the stationary and the thermodynamic equilibrium value as small as possible it is essential that growth (or melting) should occur at many crystals simultaneously and this is best achieved by thorough stirring of the system or by ensuring that no part of the liquid or solid is far from a good conducting surface. The existence of this temperature difference and the variation of this difference with rate of cooling makes it undesirable to use temperatures recorded in one laboratory for the assessment of the purity of a sample in another laboratory.

If the rate of heat removal is absolutely constant (*i.e.* if the mole fraction frozen varies linearly with time) then it is possible to analyse the freezing curves to obtain the moles per cent of impurity present. This analysis may be done algebraically or graphically[6]. However in our experience the fraction frozen rarely varies linearly with time and we have therefore adopted a procedure based upon one recommended by SCHWAB AND WICHERS[2]. These workers recommend a comparative method which is applicable even if the fraction frozen does not vary linearly with time. The freezing curves are obtained in our experiments by using a slightly modified form of the apparatus previously described[7,8]. The amount of supercooling is kept as small as possible and the results are plotted as shown in Fig. 1. The time for complete freezing is obtained graphically (see STULL[9]) as is shown in Fig. 1. The difference ($\triangle t$) between

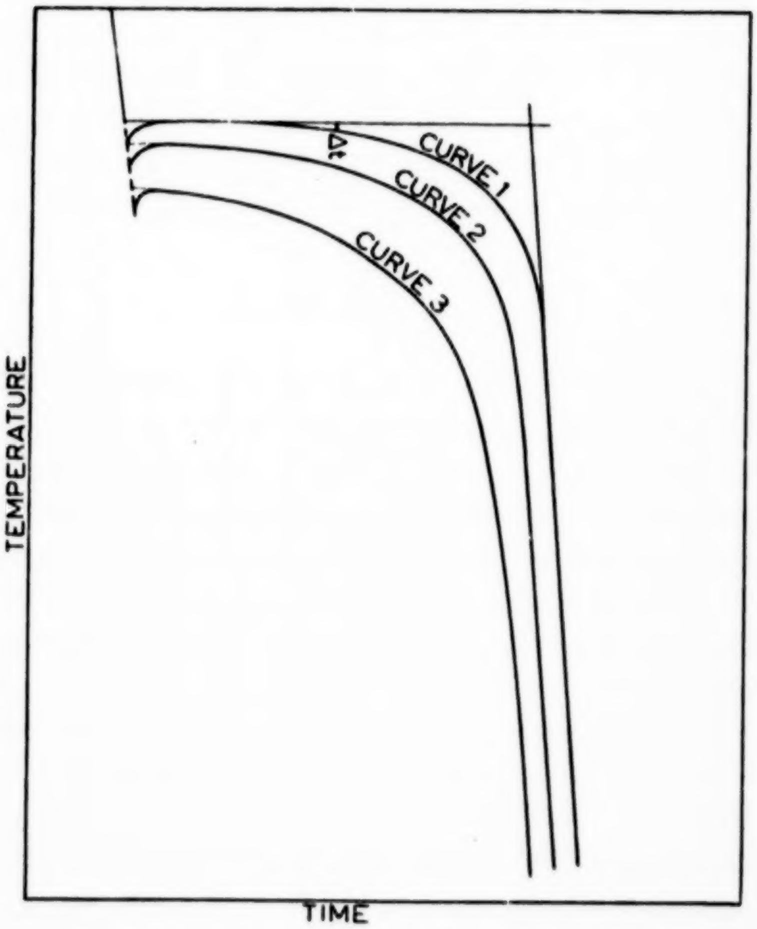

Fig. 1. Temperature-time curves obtained in freezing experiments

the initial freezing temperature and the temperature at a time equal to half that required for complete freezing is found (curve 1). A known small amount (x_1 moles per cent) of impurity is then added and another freezing curve is obtained using exactly the same rate of cooling (*i.e.* the same pressure in the Dewar, the same coolant with the same depth of immersion and the same rate of stirring) as previously. A value ($\triangle t_1$) for the difference between the new initial freezing temperature and the temperature at a time equal to half that required for complete freezing is thus obtained (curve 2). The experiment is carried out yet again after the addition of more impurity (total impurity added x_2 moles per cent) and a further value ($\triangle t_2$) determined for the temperature difference (curve 3).

If it is found that the following relation is obeyed

$$(\triangle t_1 - \triangle t)/x_1 = (\triangle t_2 - \triangle t)/x_2$$

then the amount of impurity originally present (x moles per cent) is calculated from the expression $x_1\triangle t/(\triangle t_1 - \triangle t)$. In practice the experiments are carried out in duplicate and thus the standard error can be computed[8]. The standard error is found to vary from example to example but the mean of several of our results indicates a value of approximately $\pm\, x/8$ for this quantity. If this technique is employed it is important to choose a suitable substance to add to the system. In general the melting point of this material should be not higher than the melting point of the main material and preferably the added substance should have a lower melting point. The chosen material should not form solid solutions nor should it form a compound with the main material. If the latent heat of fusion of the main material is known it is possible to check that the material used as added impurity is suitable by calculating the latent heat of fusion of the main substance from the depressions observed in the initial freezing point by the addition of x_1 and x_2 moles per cent of the impurity. If the value for the latent heat of fusion so found agrees with the value obtained by calorimetry then the choice of added impurity was suitable.

This freezing point procedure for purity determinations is the dynamic method we prefer to employ in this laboratory but some materials reach temperature equilibrium so slowly that this method cannot be used. The occurrence of these unsuitable conditions can usually be detected by studying the shape of the freezing curve, for example the rise in temperature following seeding may be very slow. Provided equilibrium is not attained too slowly it may still be possible to employ a dynamic method if a melting point procedure is used. A melting point method is also useful for studying materials which tend to form metastable crystalline forms at temperatures near the melting point.

It is of some interest to consider what properties of a substance determine the rate of attainment of equilibrium between solid and liquid. The theoretical treatment discussed by HILLIG AND TURNBULL[5] leads to the following expression for the velocity of crystallization (v) in cm/sec:

$$v = 3(\triangle S)^2\, D(\triangle T)^2/4\pi V_m RT\sigma$$

where $\triangle S$ is the molar entropy of fusion, D is the diffusion coefficient, $\triangle T$ is the undercooling, V_m is the molar volume and σ is the surface free energy. As D is approximately proportional to the inverse of the viscosity it follows that the magnitude of the viscosity at the melting temperature is an important factor in determining if a dynamic freezing point procedure can be used to estimate purity. Indeed if the viscosity of the melt is high not only will v tend to be small but difficulties may arise in securing adequate mixing of the system. As an example of these conditions it may be noted that the purity of specimens of *o*-cresol with viscosity of approximately 6 centipoises at the melting point, and specimens of *p*-cresol with viscosity of approximately 10 centipoises at the melting point can just be determined by our freezing point procedure but the purity of specimens of *m*-cresol with a viscosity of 40 centipoises cannot. Mechanical factors may also influence the speed of attainment of equilibrium in a freezing point apparatus. Thus the growth of a few large crystals may block the stirring or a dense network of crystals may obstruct liquid flow and prevent a freezing point procedure being used.

3. MELTING CURVES

Several melting point techniques have been described in the literature for the quantitative determination of purity. Thus ROSSINI and co-workers[10] advocate the use of their freezing point apparatus worked in reverse and make the assumption that the fraction melted is proportional to time. However the sudden reversal from cooling to warming conditions tends to upset all the temperature gradients within the apparatus and the readings obtained may not be easy to interpret. CARLETON[11] has described the use of an apparatus due to SMIT[12] in which an attempt is made to cause the fraction melted to be proportional to the time. However this apparatus may be difficult to manipulate if a very pure sample is under investigation because the warming of the outside bath must be suddenly stopped and the temperature maintained constant as soon as melting occurs. A melting point procedure will now be described based on the idea of comparative experiments. This experimental procedure includes, as a special case, the conditions recently treated by MATHIEU[13].

Consider a small calorimeter vessel constructed of thin metal, carrying metal vanes internally and with a thermocouple pocket up the centre. Let this vessel be enclosed in two metal sheaths with air gaps between them and let the outer sheath be heated electrically. Suppose the whole assembly is mounted in a Dewar vessel.

Consider a frozen sample within the calorimeter and suppose the outer sheath is heated at a steady rate by the passage of a steady current. The conditions can be represented in Fig. 2 where the line S represents the temperature of the inner shield and the curve A the temperature of a sample after melting has started. Consider an "equilibrium" part of the curve A. The rate, R, of adding heat to the sample is given by

$$R = K + k\delta \quad \text{(1)}$$

where K and k are constants and δ is the difference in temperature indicated on Fig. 2. The rate of change of the fraction melted $[\mathrm{d}(1-r)/\mathrm{d}\tau]$, where r is the fraction frozen and τ is the time, is proportional to the rate of adding heat, hence

$$\mathrm{d}(1-r)/\mathrm{d}\tau = K_1(K + k\delta) \quad \text{(2)}$$

where K_1 is a constant,

But if the sample is of reasonably high purity then to a good approximation

$\delta = k_1\tau$ where k_1 is a constant and τ is the time since melting started. Hence equation (3) is a good approximation to equation (2).

$$d(1-r)/d\tau = K_2 + k_2\tau \quad \ldots\ldots\ldots\ldots (3)$$

where K_2 and k_2 are constants.

Equation (4) is obtained from equation (3) by integration and by setting $\tau = 0$ for $r = 1$.

$$1-r = K_2\tau + 0.5k_2\tau^2 \quad \ldots\ldots\ldots\ldots (4)$$

Now if equilibrium between solid and liquid is obtained and the impurity is insoluble in the solid then the temperature T is related to the function $(1-r)$ by equation (5).

$$T = T_{f0} - ax/(1-r) \quad \ldots\ldots\ldots\ldots (5)$$

where T_{f0} is the freezing point of the 100% pure material, a is a constant for a given material and x is the mole per cent impurity.

Hence equation (6) is obtained by combining equations (4) and (5).

$$T = T_{f0} - ax/(K_1\tau + 0.5k_1\tau^2) \quad \ldots\ldots (6)$$

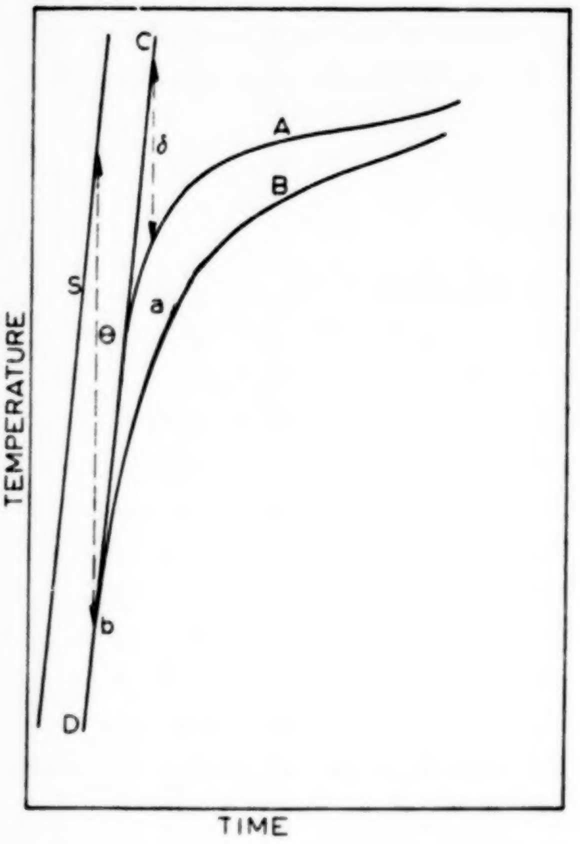

Fig. 2. Temperature-time curves obtained in melting experiments.

This equation is of little use because in general K_1 and k_1 are not known. However suppose the experiment is repeated after the addition of a known quantity of impurity (x_1 moles per cent) using the same experimental conditions, that is the same heating current, Dewar vessel etc. as formerly, then we have

$$T_1 = T_{f0} - a(x + x_1)/(K_1\tau + 0.5k_1\tau^2) \quad \ldots\ldots\ldots\ldots (7)$$

Consider the values of T and T_1 for equal values of τ then equation (8) is obtained from equations (6) and (7).

$$xT_1 = (x + x_1)T - x_1T_{f0} \quad \ldots\ldots\ldots\ldots (8)$$

Thus if T is plotted against T_1 for equal values of τ (time $\tau = 0$ at "a" on curve A and $\tau = 0$ at "b" on curve B in Fig. 2) a straight line results of slope $x/(x + x_1)$ whence x can be found since x_1 is known. In practice a further amount of impurity is added and x redetermined by the aid of the new curve. If good straight lines are obtained over a certain time interval and if the two values of x so derived are in agreement then it is suggested that reliance can be placed on the result.

In an actual experiment the line S may curve over somewhat as soon as melting commences but it follows that equation (8) is still applicable because this curvature will be nearly the same in the original experiment and in the experiment after addition of impurity. In order to determine τ it is necessary to find the point "a" on curve A where melting begins. For samples of high purity no difficulty has been experienced in locating this point. In practice the appropriate emf's of the thermocouples are plotted instead of values of T and T_1 and curves obtained in this way will be found in the paper by HANDLEY[14]. It must be emphasized that this technique yields satisfactory results for many systems where the dynamic freezing point pro-

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cedure just fails. However it is obvious that there are materials which attain equilibrium so slowly that no dynamic method of purity determination can be employed to establish their purity.

4. DIFFERENTIAL METHOD

In conclusion a different type of problem will be considered. In commerce it is usual for buyer and seller to draw up a contract agreeing on the acceptance of a batch of material provided it has a purity equal to or greater than an agreed figure. In the past these contracts were often based on the concentration of a certain specified impurity (*e.g.* water) being below an agreed amount. Recently technical developments have lead to contracts being formulated in which the total amount of impurity in moles per cent is stipulated. In such circumstances it is natural to turn to freezing and melting point procedures for the certification of specimens. However established freezing and melting point method usually require delicate and expensive apparatus unsuitable for use in a factory and therefore we have been seeking a somewhat different solution to this problem. The apparatus that has been designed consists of a cylindrical copper block drilled symmetrically with six holes. Five of these holes contain silver cylindrical vessels packed with silver gauze and each carries a thermocouple pocket. The sixth hole contains a small copper cylinder which is itself bored with six holes, five of which are occupied by the reference junctions of thermocouples the other junctions of which are in the silver cells. The outputs from these five thermocouples are fed to a six point, 1 mV recorder. The outside of the large copper block is wound with an electric heating element and the whole apparatus which is enclosed in a glass sheath can be placed within a Dewar vessel. Four of the silver cells contain specimens of the compound of unknown purities and the fifth contains the reference specimen which is of such a purity that it is just acceptable.

Consider the behaviour of one of the thermocouples as the block heated. If the curve S in Fig. 2 now represents the temperature-time relationship of the small copper block which contains the reference junctions, then the emf recorded is proportional to the temperature difference ($\Theta + \delta$), here δ is the temperature difference at any time between points on the melting curve and on C extrapolated. A typical record is shown in Fig. 3 full curve. Point "v" represents the commencement of melting, "w" corresponds to the maximum temperature difference between the cell and the reference copper block while the line "wx" shows the decrease in the temperature difference which takes place when all the sample is melted. Curve abc represents the curve for another cell containing a sample of lower purity.

Clearly four criteria can be used to differentiate between the purity of these samples.

(*i*) The sample of lower purity begins to melt first *i.e.* point "a" appears before point "v".

(*ii*) The higher the purity the more sudden is the deviation from the straight line when melting begins.

(*iii*) The more impure the sample the sooner is the maximum in the curve reached, *i.e.* "b" occurs before "w" in time.

(*iv*) The lower the purity, the lower is the height of the peak.

Since points "a" and "v" on the curve lie in the premelting region it was to be

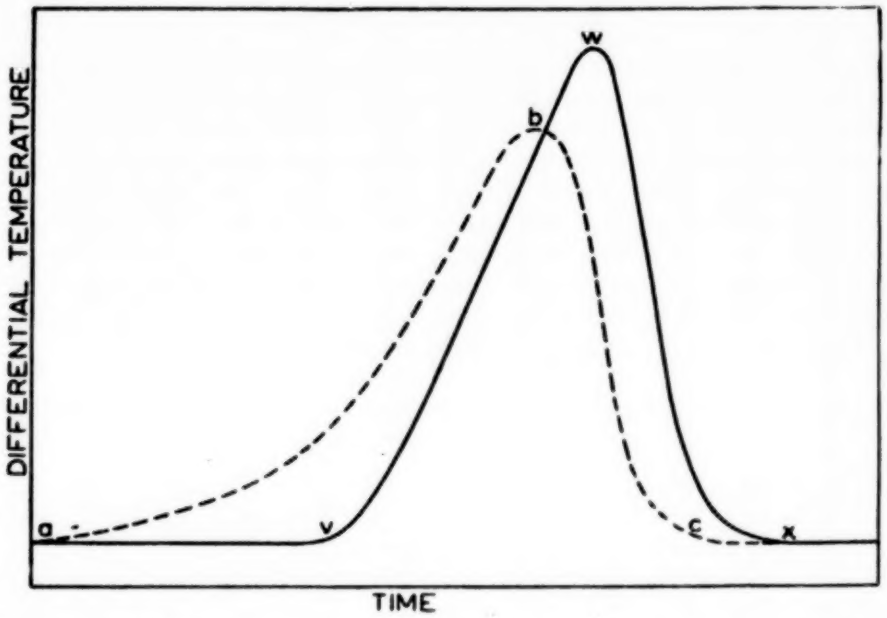

Fig. 3. Differential temperature-time curves obtained in melting experiments

expected that the curvature of this part of the graphs would provide a sensitive test for purity and this has been found to be the case experimentally.

This method for comparing the purities of samples has the following advantages.

(*a*) The apparatus is robust and is fully automatic.

(*b*) High sensitivity is achieved without the use of complicated switching gear to change the range of the recorder.

(*c*) A direct comparison is made between the unknown samples and the reference specimen.

(*d*) The method is rapid, for example four hours is required for a typical determination.

Experimental details are set out in the paper by HANDLEY[14].

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SUMMARY

Some theories of freezing and melting are considered and as a result it is concluded that the stationary temperatures observed in dynamic systems in one laboratory may not be suitable for use for the determination of purities in another. Factors which give rise to a slow attainment of equilibrium between solid and liquid are considered. The use of a comparative technique for the determination of purities by freezing point measurements is advocated and a new method for the determination of purities by melting curves is described. This method allows the purities of certain materials to be ascertained when equilibrium between solid and liquid is reached rather slowly. Finally an outline is given of the theory of a method suitable for the intercomparison of the purity of several samples simultaneously.

RÉSUMÉ

L'auteur considère quelques théories de la congélation et de la fusion et il conclut que les températures stationnaires observées dans des systèmes dynamiques dans un laboratoire peuvent ne pas être utilisables pour les déterminations de puretés dans un autre. Il considère des facteurs qui causent un établissement lent de l'équilibre entre solide et liquide. L'auteur recommande l'emploi d'une technique de comparaison pour la détermination de puretés par des mesures de points de congélation et décrit une nouvelle méthode de détermination de puretés par des courbes de fusion. Cette méthode permet de déterminer la pureté de certaines matières lorsque l'équilibre solide-liquide est atteint plutôt lentement. Finalement la théorie d'une méthode recommandable pour comparer simultanément les puretés de plusieurs échantillons est esquissée.

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ZUSAMMENFASSUNG

Einige Gefrier- und Schmelztheorien werden betrachtet und es wird geschlossen, dass die in einem Laboratorium beobachteten stationären Temperaturen dynamischer Systeme zur Anwendung für Reinheitsbestimmungen in einem anderen Laboratorium nicht geeignet sein müssen. Faktoren welche die langsame Einstellung des Gleichgewichtes zwischen der festen und flüssigen Phase verursachen, werden erörtert. Die Anwendung einer Vergleichstechnik bei Reinheitsbestimmungen mit Hilfe von Gefrierpunktsmessungen wird empfohlen und eine neue Methode für Reinheitsbestimmungen mit Hilfe von Schmelzkurven wird beschrieben. Diese Methode gestattet die Reinheit gewisser Materialien zu bestimmen wenn sich das Gleichgewicht zwischen der festen und flüssigen Phase langsam einstellt. Endlich wird die Theorie einer zum gleichzeitigen Vergleich der Reinheit verschiedener Proben geeigneten Methode umrissen.

REFERENCES

[1] W. P. White, *J. Phys. Chem.*, 24 (1920) 393.

[2] F. W. Schwab and E. Wichers, *Temperature - Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, p. 256.

[3] J. Timmermans, *Les Constantes Physiques des Composés Organiques Cristallisés*, Masson et Cie, Paris, 1953, p. 377.

[4] B. Chalmers, *J. Metals*, 6 (1954) 519.

[5] W. B. Hillig and D. Turnbull, *J. Chem. Phys.*, 24 (1956) 914.

[6] W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, 32 (1944) 197.

[7] E. F. G. Herington and R. Handley, *J. Chem. Soc.*, (1950) 199.

[8] D. P. Biddiscombe, E. A. Coulson, R. Handley and E. F. G. Herington, *J. Chem. Soc.*, 1954, 1957.

[9] D. R. Stull, *Ind. Eng. Chem., Anal. Ed.*, 18 (1946) 234.

[10] A. R. Rossini, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, 35 (1945) 355.

[11] L. T. Carleton, *Anal. Chem.*, 27 (1955) 845.

[12] W. M. Smit, *Dissertation*, Amsterdam, 1946.

[13] M. P. Mathieu, *Bull. soc. chim. Belges*, 63 (1954) 333.

[14] R. Handley, *Anal. Chim. Acta*, 16 (1957) 115.

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ERRORS OCCURRING IN THE DETERMINATION OF TEMPERATURE-HEAT CONTENT CURVES

by

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INTRODUCTION

When melting or freezing curves are used as qualitative or quantitative criteria for purity it is usually assumed that the temperature functions represented by these curves are valid under thermodynamic equilibrium conditions.

However, it must be realized that during the experimental determination of these curves heat is transported (continuously or discontinuously) to or from the sample to be investigated. Thus permanent or temporary deviations from the thermodynamic equilibrium conditions will always occur and the obtained curves will represent the desired temperature-heat content curves only approximately.

To what extent the obtained curves differ from the desired ones depends on the rates of the occurring phase transitions, the rates of heat transport and the rates of diffusion (homogeneity of the occurring phases).

These rates as such, as well as their influences, depend on the sample and on the experimental conditions.

The experimental conditions may differ widely and a quantitative treatment of the influence of all the factors mentioned soon becomes very complicated.

We shall therefore restrict ourselves to some qualitative considerations concerning the rates of phase transitions and the rates of diffusion. Subsequently the influence of heat transfer will be discussed and an approximately quantitative discussion on the temperature differences occurring with the "thin film" method will follow.

Although it is realized that the following is far from complete, some conclusions can be drawn that are applicable to a wide variety of experimental methods.

I. INFLUENCE OF RATES OF PHASE TRANSITIONS

When two phases are in thermodynamic equilibrium the amount of substance passing from phase 1 into phase 2 per unit time and unit surface area is equal to the amount of substance passing in the opposite direction. These rates cannot be measured and will be called absolute rates. The absolute rates will depend on temperature and some other factors which are not yet clearly understood. When no thermodynamic equilibrium exists the rate of the phase transition $1 \rightarrow 2$ may be larger than the rate in the opposite direction. The result will be an increase of the amount of substance contained in phase 2. This increase per unit time and unit surface area will be called the net rate of phase transition, which is zero when thermodynamic equilibrium occurs.

1.1. Solid-liquid transitions

Discussions and measurements on crystallization have been given by OSTWALD[1], TAMMANN[2], OTHMER[3], MEISSNER[4], KRAHL[5], JACKSON AND CHALMERS[6] and others.

Although the different authors do not agree completely it may be concluded from their papers that the net rate of crystallization may be low and depends on temperature.

The general picture is that the net rate of crystallization (being zero at the equilibrium temperature) initially increases at decreasing temperature and subsequently decreases after having passed through a maximum.

This somewhat peculiar behaviour of the net rate of crystallization may become more clear by considering the net rate of crystallization as the difference of the absolute rates of crystallization and melting (see Fig. 1).

This picture tallies qualitatively with the general theory on reaction kinetics. Without indulging in theoretical considerations on the kinetics of melting and crystallization we accept the drawn curve of Fig. 1 as a general representation of experimental experience. It is stressed that this curve obtains to systems in which both liquid and solid are present in *finite* quantities.

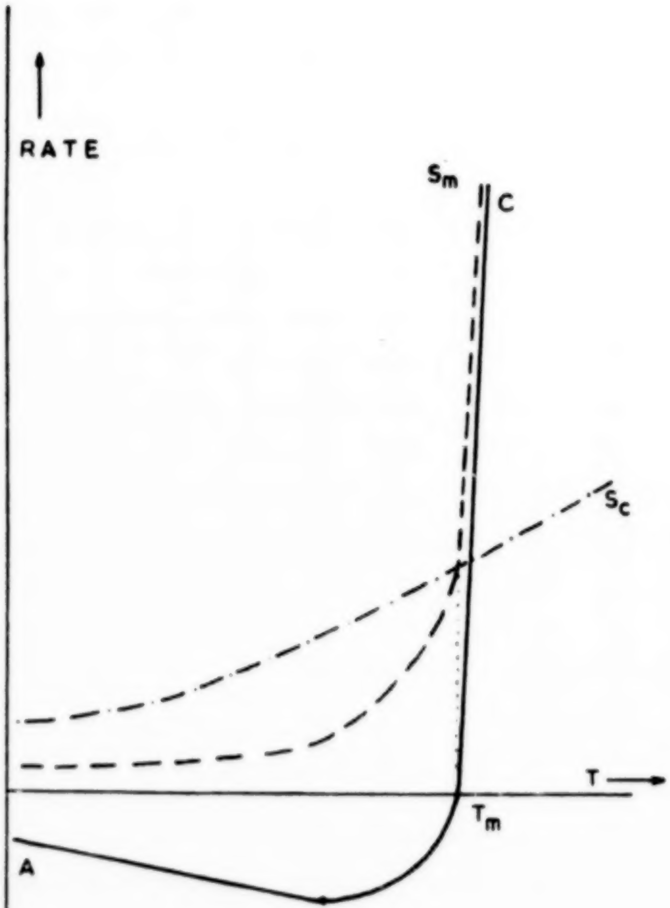

Fig. 1. Melting and crystallization rates as a function of temperature.
Curve S_c (—·—·—·): absolute rate of crystallization.
Curve S_m (— — —): absolute rate of melting.
The drawn curve represents the net rate of melting (S_m-S_c).
(A negative net rate of melting means a positive net rate of crystallization.)

As the net rate of melting may be considered as a measure for the rate of heat consumption, Fig. 1 leads to the following conclusions regarding a solid-liquid system consisting of one component.

When thermodynamic equilibrium exists the temperature of the system is T_m.

When heat is ***supplied*** to the system its temperature will increase until the net rate of melting meets the rate of heat supply. This is only possible at temperatures above T_m. Since the net rate of melting increases sharply at increasing temperatures (above T_m) the deviation from the equilibrium temperature will be low. (As a matter of fact, these deviations are imperceptible as far as is known*.)

When heat is *withdrawn* from the system its temperature will decrease until the rate of heat production (crystallization) meets the rate of cooling. This is only possible at some temperature below T_m. However, in this region the rate of heat production (crystallization) may be low and may increase only slightly at decreasing temperatures. *Consequently the temperature finally obtained may differ appreciably from the equilibrium temperature.*

The temperature finally obtained remains constant as long as the rate of heat production of the system meets the rate of cooling. This is a steady state phenomenon and has nothing to do with thermodynamic equilibrium.

The type of undercooling mentioned above will be called two-phase undercooling. It should be distinguished from the undercooling of a liquid containing no perceptible amount of solid. The latter type of undercooling (to be called monophase undercooling) demonstrates itself as the well known "undercooling peak" in a cooling curve. Monophase undercooling depends on the rate of nuclei formation, whereas two-phase undercooling is more related to crystal growth.

In our experience two-phase undercooling is considerable with quite a number of substances even at cooling rates as low as 0.3 degree centigrade per minute (*ca.* 0.1 cal per gram minute). This is illustrated by Figs. 2 and 3.

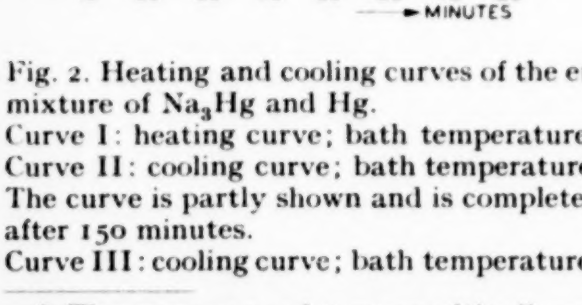

Fig. 2. Heating and cooling curves of the eutectic mixture of Na_3Hg and Hg.
Curve I: heating curve; bath temperature 25°C.
Curve II: cooling curve; bath temperature 20°C. The curve is partly shown and is completed only after 150 minutes.
Curve III: cooling curve; bath temperature 18°C.

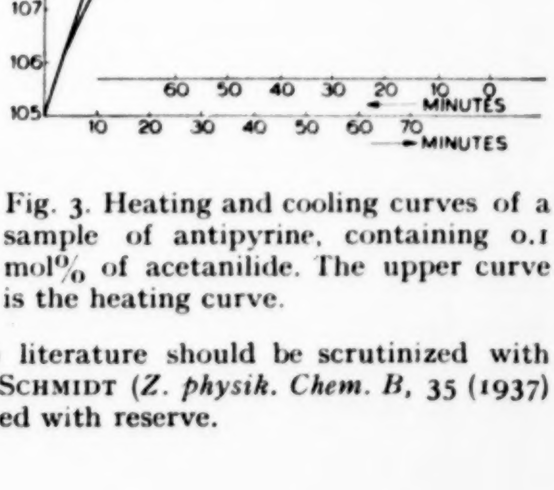

Fig. 3. Heating and cooling curves of a sample of antipyrine, containing 0.1 mol% of acetanilide. The upper curve is the heating curve.

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* The rare cases of "supermelting" mentioned in the literature should be scrutinized with great care; *e.g.* the conclusions drawn by VOLMER AND SCHMIDT (*Z. physik. Chem. B*, 35 (1937) 467) regarding the supermelting of gallium must be treated with reserve.

Fig. 2 shows heating curves and cooling curves of an exact eutectic mixture of Na_3Hg and Hg. The mixture was contained in a closed cylindrical tube provided with a thermometer well. The thickness of the cylindrical layer of metal was about 3 mm. The vessel was contained in a wide glass jacket and subsequently placed in a bath of constant temperature. The temperature of the vessel was recorded as a function of time. No stirring was applied to the sample. Curve I is a heating curve obtained after having cooled the mixture somewhat below 18°C.

The curve shows a constant temperature at 21.49°C for nearly 50 min. Complementary experiments carried out at bath temperatures as high as 30° or as low as 22°C all showed a range of constant temperature at exactly the same value of 21.49°C. As is obvious, the length of the constant range varied with the bath temperature.

On cooling, however, the constant range if present proved to be a function of the bath temperature (see Fig. 2, curves II and III).

The experiments could be repeated at choice, always yielding the same results. Additional experiments have been carried out with a sample that was partly melted. This sample was placed in a bath with a temperature either higher or lower than 21.49°C. The temperature registered fitted respectively to curve I (hot bath) or to the corresponding cooling curve (cold bath).

Comparable results have been obtained with *antipyrine*. The heating curves of this substance show a range of constant temperature at 110.45°C, which temperature appeared to be independent of the rate of heating. The cooling curves determined at a comparable rate of cooling show a small undercooling peak and subsequently the temperature rises up to a maximum at about 109°C. The height of the maximum is dependent on the rate of cooling and is always perceptibly below 110.45°C. The curves obtained are comparable with those of Fig. 3 showing heating and cooling curves of a sample of antipyrine, artificially contaminated by 0.1 mol% of acetanilide. The curves obtained have been determined with the thin film apparatus, described elsewhere[7]. With this apparatus no stirring is applied.

The cycle formed by the heating and cooling curve has been repeated several times without showing results essentially different from those represented by Fig. 3. Subsequently, experiments have been carried out with a sample that was partly melted. The temperature of this sample adapted itself to the upper or lower curve depending on whether heating or cooling was applied. All experiments were carried out with one and the same sample without removing it from the apparatus. The experiments could be duplicated with other samples.

Fig. 3 shows that a cooling curve of an impure substance may have a fairly flat part, giving the impression that the impure substance is extremely pure. The amount of contaminant calculated from the heating curve, on the contrary, tallied with the amount added.

Phenomena analogous to those represented by Figs. 2 and 3 have been obtained with *p*-xylene, benzyl benzoate and azobenzene. The literature gives evidence that quite a number of substances behave in the same way. We also observed less pronounced, though still noticeable differences between the heating and cooling curves of naphthalene. The heating and cooling curves of benzoic acid showed no differences exceeding our limit of accuracy.

1.2. Transitions in the solid phase

With a few alterations Fig. 1 may also be regarded as representing the transition rates between two solid phases which are coexistent at T_m (enantiotropy). It should be born in mind that transition rates in solids are often low. The curve S_m and consequently the part T_m-C of the drawn curve may be far less steep. In our experience this holds good for the odd fatty acids C_{13}, C_{15} and C_{17}. A heating curve usually demonstrates clearly the occurrence of enantiotropic transitions. When melting occurs before the solid-solid transition is completed the melting curve obtained is obviously unreliable. It is therefore recommended that a sample be stored for some time at a temperature somewhat above the transition temperature before proceeding to the determination of the melting curve.

Other phase transitions in the solid may be due to monotropy. Monotropy is a typical non-equilibrium phenomenon. A monotropic solid may be compared to an undercooled liquid. When it is "seeded" with the stable modification, transition into the stable form should occur. However, the transition rate is often low. Extremely low transition rates have been met with in methyl esters of palmitic and stearic acid. Metastable crystals of these esters could be stored for one year in contact with stable crystals at a temperature only 0.5° below their melting point without completing the transition into the stable form[8]. Fats may show comparable phenomena.

It may be useful to pay some extra attention to an effect caused by rapid cooling. Suppose a solid has been obtained by rapid cooling of a liquid. When a heating curve of such a solid is determined it may be unequal to the heating curve of a solid obtained from the same liquid at a moderate rate of cooling. We found this phenomenon occurring with a wide variety of substances including pure metals. This may be due either to (unknown) metastable forms of the solid or to the occurrence of imperfect crystals. The distinction is not essential; it is only mentioned as a reminder that (in order to obtain reliable melting curves) certain precautions to obtain a stable solid should not be omitted, not even when no metastable forms of the solid are known.

Storage of the solid at a temperature slightly below the melting point counteracts all the effects mentioned in this section. In many cases storage of the solid at elevated temperature for about an hour will do. Fatty acids appeared to need several days, and with fatty acid methyl esters no satisfying results could be obtained. It may be that many long-chain compounds display analogous difficulties.

On the strength of the facts mentioned above it may be advisable to submit an obtained heating curve to an internal check (see below), if necessary combined with duplicate measurements under different experimental conditions.

2. INFLUENCE OF THE RATES OF DIFFUSION

When the solid and the liquid of a multicomponent system are in thermodynamic equilibrium the composition of the solid will usually differ from that of the liquid. When such a system is submitted to further crystallization or melting, the composition of at least one of the phases will change *in the vicinity of the contact surface.*

Consequently, the bulks of the phases are not coexistent. Diffusion tends to equalize the concentration differences occurring both in the solid and in the liquid phase and should therefore be promoted. This can be done by spreading the phases in thin layers and/or by stirring.

2.1. The effect of stirring

It should be noted that stirring as such promotes the homogeneity of only the liquid phase. It does not affect inhomogeneities occurring in the solid. Thus even when stirring is applied thick layers may be disadvantageous. An advantageous effect of stirring is that it may cause disintegration of solid particles, thus producing a larger contact surface which also promotes the bulk rate of crystallization (see section 1).

However, this advantage is somewhat dubious. First it should be noted that stirring is only applicable in a limited range of solid to liquid ratios. Further, the effectivity of stirring (when possible) depends on the amount of solid present. Thus an extra variable factor is introduced. Influence of the way and rate of stirring on the obtained curves may be demonstrated by examples derived from the literature.

When the effect of low *crystallization* rates is accounted for (see section 1) it is not surprising that cooling curves appear to be more dependent on the way of stirring than heating curves.

3. INFLUENCE OF THE RATE OF HEAT TRANSPORT

When heat is supplied to or withdrawn from a calorimeter, temperature differences will occur throughout all parts of the calorimetric system, including the wall, the substance contained in it, and even the thermometer. These differences again constitute a source of errors. The errors depend on the rate of heating, the sizes of the parts of the system and the heat conductivities of the composing materials.

An attempt will be made to obtain an impression of the size of these errors. We therefore give the calculations carried out to obtain the allowable dimensions of the thin film apparatus[7,8].

With the thin film apparatus heat is supplied to a cylindrical measuring vessel schematically represented by Fig. 4. The substance to be investigated is contained in the annular space (2) between the outer wall of the thermometer (1) and the inner wall of the glass vessel (3). The heat supply (or withdrawal) is constant and occurs from the outside of the glass vessel (3).

The calculations necessary for evaluating the occurring temperature differences before melting sets in differ from those during the melting process. They will be presented subsequently.

The calculations are restricted to the cylindrical part of the system. The flow of heat through the top and the bottom of the system is disregarded.

The following symbols will be used:

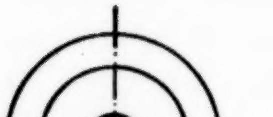

Fig. 4. Measuring vessel with thermometer.

a	temperature conductivity (λ/h) in cm^2/sec
$C_1, C_2 \ldots . C_f, C_m$	constants

d	thickness of a layer
$\triangle$	temperature difference, defined by equation (5)
f	fraction of $\triangle$ such that $\triangle \cdot f$ is the temperature accuracy aimed at
H_n	heat content per unit length of a cylinder with radius r_n (cal/cm² degree)
h	specific heat of a substance per unit volume (cal/cm³ degree)
K	rate of heating or rate of heat supply per unit volume (degree/sec or cal/cm³ sec)
k	integration constant
l	length of a cylinder
λ	heat conductivity (cal/cm² sec degree)
n	index referring to the nth layer of substance
p	mol percentage of a contaminant present in a sample
r	radius
S	heat of fusion per unit volume (cal/cm³)
T	temperature (degree centigrade); T_s melting point of a pure substance
t	time (seconds); t_s total time necessary to melt a given sample at a rate of heat supply K
Y	fraction of sample melted
Y_i	fraction melted before a curve has become reliable

3.1. Temperature differences occurring before melting sets in

It is assumed that constant heat supply to the system has already been switched on for a sufficiently long time. Then the temperature of each part of the system will rise at a constant rate K.

According to Fourier:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_r = a_n \left(\frac{\mathrm{d}^2T}{\mathrm{d}r^2}\right)_t \qquad (1)$$

where a_n stands for the temperature conductivity of the substance present at r.

Substitution of $\frac{\mathrm{d}T}{\mathrm{d}t} = K$ and integration leads to

$$a_n \cdot \frac{\mathrm{d}T}{\mathrm{d}r} = Kr - k_{n\text{-}1} \qquad (2)$$

where $k_{n\text{-}1}$ is a constant which is determined in the following way. Layer n is enclosed between two cylinders with radii $r_{n\text{-}1}$ and r_n. The amount of heat passing per unit height and unit time through a layer of infinitesimal thickness dr at $r_{n\text{-}1}$ equals the product of the rate of heating and the heat capacity ($H_{n\text{-}1}$) of the cylinder with radius $r_{n\text{-}1}$ and with unit height.

Thus:

$$KH_{n\text{-}1} = 2\pi r_{n\text{-}1}\,\lambda_n \left[\frac{\mathrm{d}T}{\mathrm{d}r}\right]_{r_{n\text{-}1}} \qquad (3)$$

Combination of the equations (2) and (3) yields:

$$k_{n\text{-}1} = K\left(r_{n\text{-}1} - \frac{H_{n\text{-}1}}{2\pi r_{n\text{-}1} h_n}\right) \qquad (4)$$

Hence the constant $k_{n\text{-}1}$ may be different in each layer of substance. Integration of equation (2) leads to:

$$a_n\,(T_{r_n} - T_{r_{n\text{-}1}}) = \tfrac{1}{2}K(r^2_n - r_{n\text{-}1}{}^2) - k_{n\text{-}1}(r_n - r_{n\text{-}1}) \qquad (5)$$

or

$$a_n\,(T_{r_n} - T_{r_{n\text{-}1}}) = \tfrac{1}{2}K(r_n - r_{n\text{-}1})\left(r_n - r_{n\text{-}1} + \frac{H_{n\text{-}1}}{\pi r_{n\text{-}1}\cdot h_n}\right) \qquad (5a)$$

In many cases the factor $H_{n\text{-}1}/\pi r_{n\text{-}1}\, h_n$ approaches to $r_{n\text{-}1}$ and the following equation holds good approximately:

$$a_n\,(T_{r_n} - T_{r_{n\text{-}1}}) = \tfrac{1}{2}K(r_n - r_{n\text{-}1})r_n \qquad (6)$$

Thus it appears that the temperature difference occurring within the layer of material to be investigated is proportional to the rate of heating, to the thickness of the layer and roughly to the diameter of the cylinder. Equation (5) may also be used to calculate the lag of the thermometer.

An impression of the occurring temperature differences may be obtained from the following example. Let $a_n = 7.5 \cdot 10^{-4}$ cm²/sec (which is an acceptable value for organic substances) and $K = 0.01$ degree/sec, $r_n - r_{n-1} = 0.1$ cm and $r_n = 1$ cm; this yields when substituted in equation (6):

$$T_{r_n} - T_{r_{n-1}} = 0.67 \text{ degree centigrade.}$$

With the thin film apparatus r_n is about 0.3 cm and the rate of heating usually applied is 0.005 degree/sec (0.3° per min). This reduces the occurring temperature difference (before melting sets in) to 0.1 degree centigrade.

At the same rate of heating the temperature difference occurring through the glass wall of the measuring vessel (wall thickness 0.4 mm) amounts to about 0.01°, and the temperature difference through the mercury thermometer also amounts to about 0.01°.

These temperature differences remain constant until the substance shows a phase transition.

3.2. Temperature differences during the process of melting

The temperature differences discussed above reveal themselves when melting starts. Melting starts at the inner wall of the glass vessel and subsequently proceeds to the thermometer. As soon as melting starts the flow of heat to the thermometer decreases appreciably. It is not reduced to zero because the temperature of the thermometer is below the temperature of the melting zone. The difference between the temperature indicated by the thermometer and the temperature of the melting zone constitutes an error gradually decreasing with time. This error suggests non-isothermal behaviour of an isothermal process. The deviations will be large at the start of the "melting range" of the curve and gradually approach zero when the curve is continued. It is important to know within what time this error has decreased to a value not exceeding the limit of accuracy aimed at. (This limit may be given by the sensitivity of the thermometer.)

The exact calculation of this time constitutes a very complicated problem. The problem becomes somewhat more simple when the following additional assumptions are introduced:

> The substance investigated is absolutely pure.
>
> The thermometer has the same thermal properties as the substance. At the moment melting sets in the temperature throughout the solid cylinder of substance is $T_s - \triangle$, where T_s is the melting point of the substance and $\triangle = Tr_1 - Tr_2$ as obtained from equation (5).
>
> The temperature at r_2 remains constant and is equal to T_s.

This problem has been treated by WILLIAMSON AND ADAMS[9]. According to these authors the temperature T present at the core of the cylinder at a time t (being zero when melting starts) is determined by the following equation:

$$\frac{T_s - T}{\triangle} = 2 \sum_{m=1}^{m=\infty} \frac{1}{R_m J_1(R_m)} \exp \left[\frac{a R_m^2}{r_2^2} t \right] \qquad \ldots\ldots\ldots\ldots \quad (7)$$

The values of R_m are the roots of the Bessel function $J_1(x) = 0$,

where $J_1(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2.4^2} - \frac{x^6}{2^2.4^2.6^2} + \ldots\ldots\ldots\ldots\ldots\ldots$

For further details reference is made to the original paper[9]. For a number of cases WILLIAMSON AND ADAMS have calculated the value of $\frac{T_s - T}{\triangle}$ as a function of at/r^2.

The first column of Table I gives the values of at/r^2 and the other columns give the appertenant values of $(T_s - T)/\triangle = f$ belonging to the bodies mentioned in the caption. With the aid of this table the time t_i necessary to reduce the original temperature difference to an allowable fraction (f) of it may be determined for a given case.

TABLE I

$\frac{at}{r^2}$	$(T_s-T)/\triangle = f$		
	cylinder with $l = \infty$	*cylinder with* $l = 2r$	*sphere*
0	1.0000	1.0000	1.0000
0.032	0.9990	0.9988	0.9975
0.080	0.9175	0.8947	0.8276
0.100	0.8484	0.8054	0.7071
0.160	0.6268	0.5301	0.4087
0.240	0.3991	0.2802	0.1871
0.320	0.2515	0.1453	0.0850
0.800	0.0157	0.0028	0.0007
1.600	0.00015	—	—

This time as such is important, *e.g.* when a static calorimetric method is used.

With dynamic methods it is more important to know the ratio (Y_i) of this time and the total time of melting t_s. This ratio Y_i determines which fraction of the substance has already melted before the obtained curve has become reliable.

With the thin film apparatus the total time of melting is determined by the following equation

$$t_s KH_{n+1} = (r_n^2 - r_{n-1}^2)S \ldots\ldots\ldots\ldots \quad (8)$$

KH_{n+1} represents the heat supplied per unit time and per unit length to the calorimetric vessel and its contents. As S is the heat of fusion per unit volume the right hand member of the equation represents the total heat necessary to melt the contents of an annular space with radii r_n and r_{n-1} and unit height.

Solving t_s from equation (8) and bearing in mind that $t_i/t_s = Y_i$ we may put

$$Y_i = t_i KH_{n+1}/(r_n^2 - r_{n-1}^2)S \quad \ldots\ldots\ldots\ldots \quad (9)$$

This equation will now be discussed.

As already stated, the time t_i may be derived from Table I. Looking at Table I we see that f is only 0.00015 at a value of at/r^2 equal to 1.600. When at/r^2 decreases only 50% (to 0.800) the value of f is multiplied by a factor 100.

As $\triangle$ may vary between about 0.1 and 1 degree centigrade we are quite on the safe side of the temperature accuracy ($f\cdot\triangle$) by choosing a value of $at/r^2 = 1.6$ (or larger); this value is not much too large because of the rapid increase of f as compared to the decrease of at/r^2. Consequently we take $t_i = 1.6\ r^2/a$.

In order to obtain a more convenient expression than equation (9) the following approximations are introduced.

The heat of fusion S is made equal to 100 times the mean specific heat of the calorimetric vessel and its contents.

Thus:

$$H_{n+1} = 10^{-2}\,\pi r_{n+1}{}^2 S.$$

Further $r_n{}^2 - r_{n-1}{}^2$ is made equal to $2r_n d$ where $d = r_n - r_{n-1}$ and quotients of r_n and r_{n+1} or r_{n-1} are assumed to be equal to unity.

Allowing these approximations and substituting the values of t_i, S and H chosen leads to:

$$Y_i = 8 \times 10^{-3}\, Kr^3/ad \qquad (9a)$$

Equation (9a) constitutes a more simple relation between Y_i, the radius of the vessel, the thickness of the layer, the rate of heating and the temperature conductivity. The temperature conductivity of a pure organic substance may be put as $7.5 \cdot 10^{-4}$ cm²/sec. Choosing the rate of heating 5.10^{-3} degree/second, $d = 0.2r$ and $r = 0.3$ cm yields Y_i = *ca.* 2%. The dimensions mentioned refer to the thin film apparatus. The formulae show that large errors may occur when deviations of the conditions occur. It may be useful to remember that an impure substance showing a wide melting range may be considered as a substance with an apparently increased specific heat, which results in a lower temperature conductivity.

3.3. Influence of contact between layers

With the above derivation it has been assumed tacitly that a perfect contact exists between the glass wall, the substance and the thermometer. Actually this contact is never completely perfect, thus causing extra temperature differences. Since the contact improves as soon as some liquid has been formed peculiar effects may result. Two cases may be distinguished: The first case concerns an ideal dynamic calorimeter showing no other flow of heat than from the outside to the core. When the substance is still entirely solid and imperfect contact exists (between the wall of the measuring vessel and the substance) a rather high temperature difference will occur between wall and substance. When melting starts the contact is improved and a higher flow of heat will result. Thus when an impure substance is investigated the initial range of premelting will be passed with a variable flow of heat, making the first part of the melting traject of the curve unreliable.

The second case deals with a non-ideal calorimeter in which an extra flow of heat occurs along the "stem" of the thermometer to or from the environment. When heat flows from the environment along the "stem" to the "bulb" of the thermometer and subsequently to the substance the temperature of the thermometer will be high when imperfect contact exists between substance and bulb. When after some melting has occurred the contact is improved the temperature of the bulb will adapt itself to that of the substance. The result will be a curve comparable with that represented in Fig. 5. Such curves have been actually obtained with some metals and organic materials that have a tendency to form large crystals. The curve represented has been obtained with sodium as substance and a tenfold thermocouple as thermometer. It could be shown that the "hill" occurring in the curve depended on the flow of heat through the couple wires.

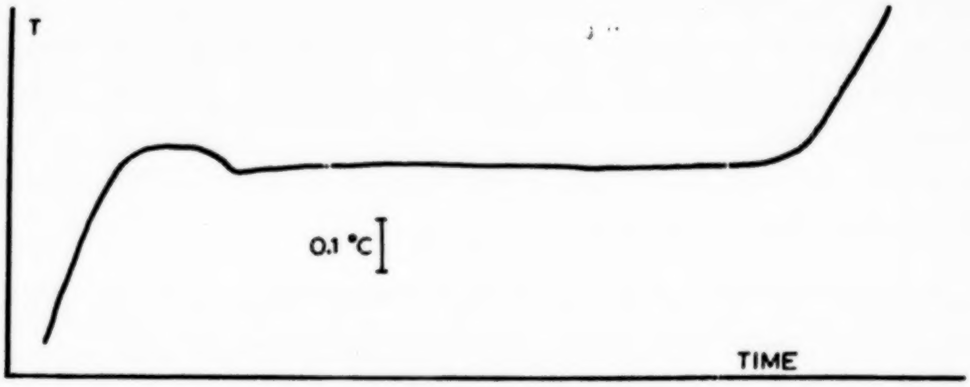

Fig. 5. Anomalous heating curve.

With mercury thermometers comparable results may be obtained. In this case the "hill" may also be due to pressure on the thermometer bulb initiating from the way of fitting the apparatus. When the substance melts the pressure is released and the bulb will resume its original volume.

4. INTERNAL CHECK ON HEATING CURVES

Realizing that quite a number of errors may have affected the obtained curve it may be very useful to apply a check on the obtained results. This may be done by duplication or triplication of the measurements under different experimental conditions.

Apart from these experimental checks one may examine to what extent a curve or a series of curves obeys the following equation:

$$T_y = T_a - \frac{C_f C_m}{C_f + Y(C_m - C_f)} \cdot p \quad \ldots\ldots\ldots\ldots\ldots \quad (10)$$

where T_y is the temperature at which a fraction Y of the substance has melted. T_a is the (unknown) melting point of the absolutely pure substance. C_f and C_m are constants and p is the mol percentage of a distinct contamination present in the sample. This equation has been derived previously[7] and will not be discussed now.

Equation (10) may be rewritten:

$$T_y = C_1 - \frac{C_2}{C_3 + Y} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

where C_1, C_2 and C_3 are constants.

These constants may be resolved algebraically by selecting three pairs of corresponding values of T_y and Y. (With the curves obtained with the thin film apparatus it proved to be advantageous to select values of Y lying closely together near $Y = 0.15$, *e.g.* $Y = 0.10$, $Y = 0.15$ and $Y = 0.20$.)

Now T_y values of the melting curve are plotted as a function of $\frac{1}{C_3 + Y}$. The plotted points should fit to a straight line with slope C_2. The ranges of Y where the plotted points deviate from the straight line should be considered as less reliable. (When the contaminant is immiscible with the main component in the solid state C_3 reduces to zero.)

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5. DISCUSSION AND RECOMMENDATIONS

The methods for determination of temperature-heat content curves may be divided into *static* and *dynamic* ones.

When a static method is applied each period of heat supply to the substance is followed by a period of "adiabatic conditions" sufficiently long to approach equilibrium to a desired extent.

When a dynamic method is applied a continuous flow of heat occurs through the substance during the determination.

With a static method the errors previously mentioned may be reduced to any desired extent provided sufficient time is available. However, it has to be realized that the longer the time necessary to approach equilibrium, the more severe are the demands on the adiabatic properties of the calorimeter. The considerations and calculations given in the preceding sections may be useful for estimating the time necessary for an accurate determination.

More simple apparatuses can be used and much time can be saved by applying a dynamic method. With dynamic methods certain precautions are imperative, however.

On the strength of section 1 it is recommended that heating curves be preferred to cooling curves.

Before starting the measurement of a heating curve the solid should be preferably kept at a temperature slightly below the initial melting point for at least one hour.

Accepting that heating curves should be preferred to cooling curves leads to doubts concerning the advantages of the stirrer method.

As the thin film method may be applied to small samples (even as small as 20 mg, which constitutes an important advantage) a comparative investigation concerning the stirrer method and thin film method is recommended.

On the strength of section 3 it is recommended that more attention be paid to the adaptation of the dimensions of the apparatuses and the rate of heating to the accuracy aimed at.

If necessary, the rate of heating should be decreased when substances with low heats of fusion have to be investigated.

With dynamic methods lack of equilibrium cannot be avoided at the very beginning and at the very end of the melting range. Even with static methods it is difficult to avoid comparable errors. Moreover, both methods may yield less reliable results when unforeseen slow processes of recrystallization occur. Therefore one is advised to subject any obtained curve to an internal check and to select a reliable part for purity determination. The internal check given in section 4 might be improved.

ACKNOWLEDGEMENT

We wish to thank Mr. H. F. VAN WIJK for his skilful experimental work.

SUMMARY

In the determination of temperature-heat content curves errors may occur which are due to low transition rates, low diffusion rates and low rates of heat transfer. These errors are subsequently discussed. Liquid to solid transitions may be slow even when liquid and solid are in contact with each other at finite ratios. This causes appreciable differences between melting temperatures and solidification temperatures. The phenomenon is called two-phase undercooling. When two-phase undercooling occurs the cooling curve obtained may lead to erroneous conclusions, *e.g.* an impure substance may seem to be extremely pure. This is illustrated by experiments.

As far as is known two-phase super*heating* appears to be negligible under normal conditions. Therefore heating curves are preferred to cooling curves.

As stirring cannot promote diffusion in the solid phase it is doubted whether the stirrer method has advantages over the thin film method.

Errors due to limited heat transfer and occurring with the thin film method have been calculated. Formulae have been given relating the dimensions of a thin film apparatus and the rate of heating to the accuracy aimed at.

Application of an internal check on heating curves is recommended.

RÉSUMÉ

Lors de la détermination des courbes température enthalpie des erreurs peuvent se produire, erreurs dues à de faibles vitesses de transition, de diffusion et de transmission de chaleur. Ces erreurs sont discutées. Les transitions liquide-solide peuvent être lentes même lorsque liquide et solide sont en contact dans des proportions finies. Ce fait cause des différences considérables entre les températures de fusion et de solidification. Ce phénomène est indiqué comme surfusion à deux phases. Lorsqu'il y a surfusion à deux phases, la courbe de refroidissement obtenue peut conduire à des conclusions erronnées; elle peut par exemple faire juger extrêmement pure, une substance impure. Des expériences illustrent ce phénomène.

Tant que l'on sache, le surchauffage à deux phases semble être négligeable dans des conditions normales. C'est pourquoi les courbes de chauffage sont préférées aux courbes de refroidissement.

Comme une agitation ne peut pas promouvoir la diffusion dans la phase solide, il est douteux que la méthode à agitation présente des avantages par rapport à la méthode à film mince.

L'auteur a calculé les erreurs dues à une transmission de chaleur limitée et qui ont lieu lors de l'emploi de la méthode à film mince. Il donne des formules reliant les dimensions d'un appareil à film mince et la vitesse de chauffage à la précision désirée.

L'application d'une méthode de contrôle par correlation aux courbes de chauffage est recommandée.

ZUSAMMENFASSUNG

Bei der Bestimmung von Temperatur-Wärmeinhalt-Kurven können Fehler auftreten, die auf niedrige Übergangs-, Diffusions- und Wärmeübergangsgeschwindigkeiten zurückzuführen sind. Diese Fehler werden erörtert. Übergänge vom flüssigen in den festen Zustand können langsam stattfinden, auch wenn Flüssigkeit und fester Stoff in endlichen Verhältnissen miteinander in Kontakt sind. Dies verursacht merkliche Unterschiede zwischen den Schmelz- und Erstarrungstemperaturen. Die Erscheinung wird Zweiphasenunterkühlung genannt. Bei Zweiphasenunterkühlung kann die Abkühlungskurve zu fehlerhaften Schlüssen führen, wie, zum Beispiel, dass eine unsaubere Substanz für äusserst rein angesehen wird. Dies wird durch Versuche dargelegt.

Soviel man weiss, scheint die Zweiphasenüberhitzung unter normalen Bedingungen vernachlässigbar zu sein. Darum sind Erhitzungskurven den Abkühlungskurven vorzuziehen.

Da man durch Rühren die Diffusion in der festen Phase nicht befördern kann, wird bezweifelt, dass die Rührmethode gegenüber der Dünnfilmmethode Vorteile bietet.

Fehler die auf beschränkten Wärmeübergang zurückzuführen sind und bei der Dünnfilmmethode auftreten, wurden berechnet. Formeln welche die Dimensionen eines Dünnfilmapparates und die Erhitzungsgeschwindigkeiten mit der erwünschten Genauigkeit in Verbindung bringen werden mitgeteilt.

Die Anwendung einer Korrelationskontrolle auf die Erhitzungskurven wird empfohlen.

REFERENCES

[1] W. Ostwald, *Z. physik. Chem.*, 21 (1897) 289.

[2] G. Tammann, *Z. physik. Chem.*, 23 (1897) 326; 25 (1898) 472; 26 (1898) 306; 29 (1899) 52; 81 (1912) 171.

[3] P. Othmer, *Z. physik. Chem.*, 91 (1915) 209.

[4] F. Meissner, *Z. anorg. Chem.*, 110 (1920) 169.

[5] M. E. Krahl, *J. Am. Chem. Soc.*, 55 (1933) 1425.

[6] K. A. Jackson and B. Chalmers, *Can. J. Phys.*, 34 (1956) 473.

[7] W. M. Smit, *Rec. trav. chim.*, 75 (1956) 1309.

[8] W. M. Smit, *A tentative investigation concerning fatty acids and fatty acid methyl esters*, Thesis, Vrije Universiteit, Amsterdam, 1946.

[9] E. D. Williamson and L. H. Adams, *Phys. Rev.*, 14 (1919) 99.

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CALCULATION OF CRYOSCOPIC DATA

by

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The usual body of data obtained during a typical freezing run for the determination of purity contains many more values than would theoretically be needed for a perfect calculation — provided, of course, that the cryoscopic constant is known and that conditions of ideality govern. It is the purpose in this paper to explore means of making more use of these data and also of the information which it is possible to extract from temperature changes that occur during the fraction of a minute following nucleation.

Analyses of purity by cryometric methods are of course subject to the errors that originate in deviations from ideality or uncertainty of the cryoscopic constant as they apply to particular contaminating agents. These can largely be limited by utilizing the technique of SCHWAB AND WICHERS*, which depends on the addition of known amounts of additional contaminant. Some of the greatest problems, however, arise because none of the measurements obtained in practice can be implicitly trusted. When a freezing curve is obtained, the values wander for many reasons — the temperature in the entire system is not uniform, there are defects of thermometry originating in a wide variety of causes, the effects of initial supercooling are never fully eliminated from the time-temperature trace, solid phase forms on the surface of the vessel and is occasionally dislodged, the volume of the condensed phase changes with an attendant change in the heat transfer, or the heating caused by the energy of stirring increases in unpredictable manner while the slurry thickens. Our problem therefore is often that of determining the curve to which our data correspond.

It is possible to take a spline, draw a curve that lies within the assumed uncertainties of the data and assume that certain points on the artificial curve represent true values from which the initial freezing point and the freezing point of the ideally pure substance can be computed. Or all the data can be submitted to instrumental calculation. The troubles, it seems to me, are that the spline technique fails to take cognizance of the fact that there is a very real theoretical curve that somehow underlies the data and that the mathematical machine must exercise an uncommon degree of judgment in accounting for departures from the calculated form. Until we learn how better to instruct the machines, it does not seem that this approach can serve much better than it does today. For the spline method I see no hope of improvement.

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* F. W. SCHWAB AND EDWARD WICHERS, *Temperature — Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, N.Y., 1941, p. 256.

Optical fitting with a perfect hyperbola

Let us tentatively employ the generally acepted approximation that Φ, the amount by which the temperature is lower than the freezing point of the theoretically pure material, is inversely proportional to t, the time that would elapse until the sample would be totally frozen:

$$\Phi = \frac{a}{t}$$

This, the equation of an equilateral hyperbola, Fig. 1(0), has only one coefficient, a, which includes the size and latent heat of sample, the rate of heat transfer, and other things. Graphically, this coefficient determines only one matter — the scale. If we magnify or shrink any prototype equilateral hyperbola, it can exactly conform to any other equilateral hyperbola. The equation does not exactly comply with a perfect actual experiment, however, to the extent that effects caused by heat capacity of solid and liquid phases and of the apparatus cause the nearly vertical asymptote to have somewhat less than infinite slope. This departure from vertical is small, so that only minor improvements are accomplished by using the theoretical slope. Since the adjustment is very easy, however, there is no reason to avoid introducing it. Hyperbolas with one horizontal asymptote and decreasing slope of the final asymptote are represented in Fig. 1. The nearly vertical asymptotes in curves 1 to 5 have slopes of 400, 200, 100, $66^{2}/_{3}$, and 50. Because the heat capacity of the solid is never larger than that of the liquid, the final asymptote is as steep as or steeper than the curve during the period that precedes freezing. Hyperbolas with increasing slope of the final asymptote are represented. The prefreezing slope can be used to select a suitable hyperbola.

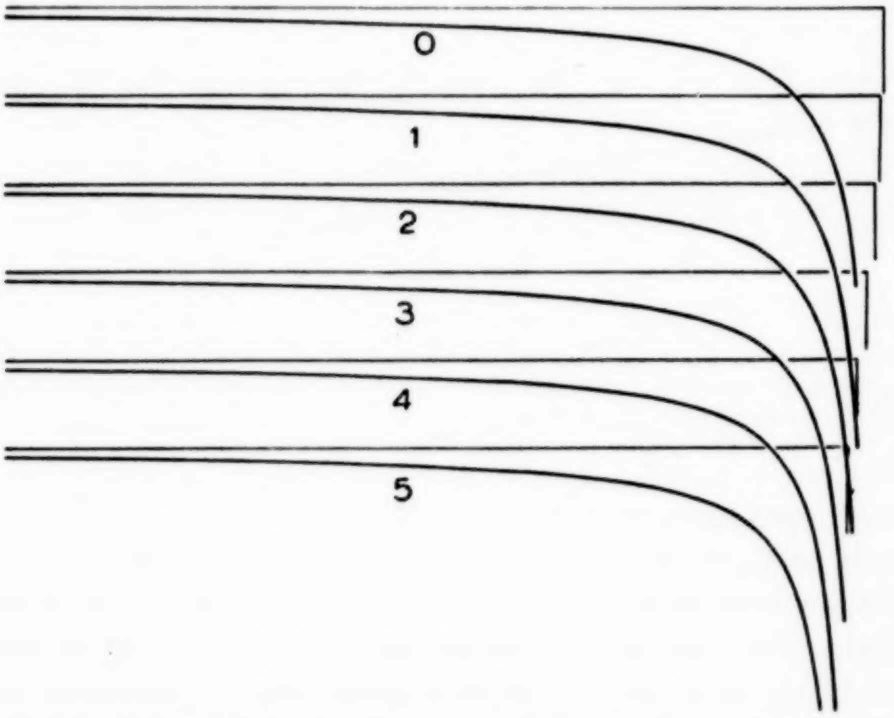

Fig. 1. Family of hyperbolas. Slopes of final asymptotes, represented by the nearly vertical slopes at the right, are as follows: (0), (1) 400, (2) 200, (3) 100, (4) 66.67, (5) 50.

Let us take the data from an excellent determination, Fig. 2, and with a photo-enlarger, lantern projector, or autofocusing lens project upon their plot the hyperbola with final slope equal to or greater than the prefreezing slope. We get a line, which is more curved than any reasonable representation of the data and displaced both vertically and horizontally. These matters can be adjusted. We must take account of the fact that, except for instrumental fluctuations and until an unwarranted amount of solid forms on the walls of the vessel or the effective viscosity increases, the true curve, if anything, will lie above the data. By changing the magnification at the enlarger and shifting the image horizontally and vertically, it is possible, as in Fig. 2, to make the superimposed curve faithfully correspond to a large part of the data.

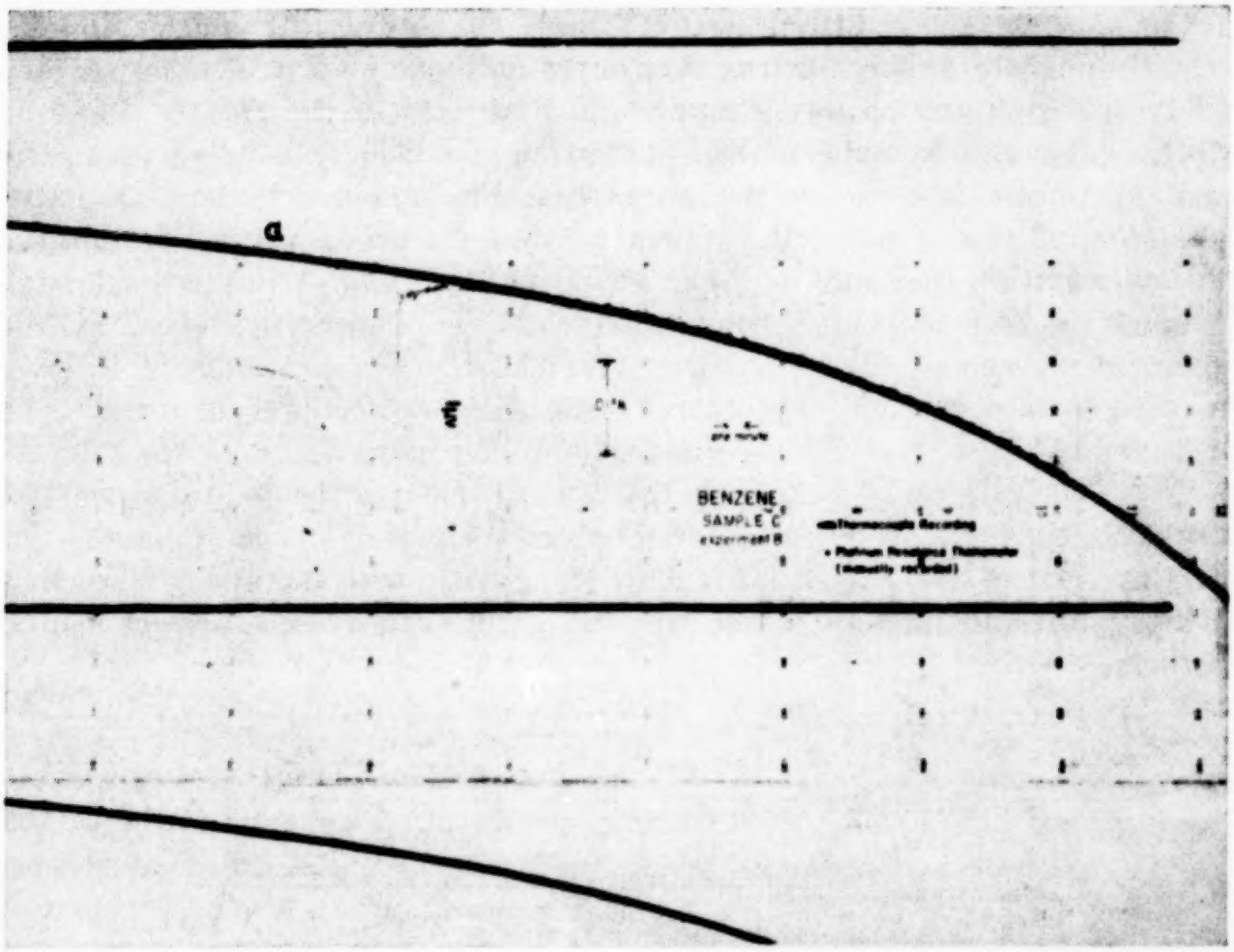

Fig. 2. Freezing curve with optically superimposed hyperbola. The projected hyperbola, a, was magnified optically so that it had the correct scale (curvature) and adjusted horizontally. It can be seen that it should be moved upward further so as to conform to those parts of the data where failure to recover from supercooling is minimal.

The only constraints utilized in the foregoing superposing of a line upon data have been that the curve represent a true hyperbola with one horizontal asymptote and a final asymptote approximately parallel to the prefreezing slope. From it the value of the horizontal asymptote, equivalent to the freezing point of the ideally pure substance, and the intercept with the prefreezing curve can be learned. If, however, we know the perfect freezing point from other sources, this provides another constraint and causes us to shift the hyperbola slightly with a presumption of more perfect determination of the theoretical temperature of first freezing. Similarly if we can calculate the time at which freezing of the perfectly pure substance would be completed, another constraint, the position of the final, nearly vertical asymptote can add to the controls. The imposition of these additional constraints does not make it necessary to shift the hyperbola much when good data are available from any experiment. Indeed the slight shifts that may be found lend more confidence to the initial setting and the validity of primary data.

It is evident that in the first part of the freeze the data lie significantly below the curve. Recovery from supercooling is incomplete. And often toward the end of a run, the data veer upward, presumably because of formation of solid on the walls and the increased energy of stirring. It is necessary to postpone, pending further studies, serious consideration of the upward trend that occurs at the end of the useful part of a run but it is possible very realistically to make a correction of the curves for the effect of supercooling.

Supercooling

It is evident that, after supercooling has taken place, the temperature will never fully recover. Indeed, for crystals to grow and by their growth provide the restorative energy to raise the temperature, the temperature must lie below that for equilibrium. It is reasonable to assume that at any moment the rate of recovery from supercooling will be proportional to some power, possibly fractional of the amount, Θ, by which the temperature lies below the unknown temperature of equilibrium

$$\frac{d\Theta}{dt} = -m\Theta^{\varrho} \qquad (1)$$

This will be modulated, of course, by the changing size of the crystals, by the decreasing viscosity with rising temperature, and by the changing composition of the liquid phase. The latter two can be disregarded in the temperature and composition ranges that interest us, and consideration of the effect of changing size of crystals can be postponed a little.

It is attractive and at first sight it appears correct to assume that ϱ is 1 — that the rate of recovery is proportional to the amount of undercooling. This integrates easily and the exponential integral lends itself to simple algebraic computation. We have made dozens of records of the recovery from supercooling with benzene, which recovers rapidly, and with titanium tetrachloride, which recovers more slowly. Over the middle course of this recovery, the curve of which Fig. 3 is representative, conforms superficially to the exponential form. It is quickly evident that this is not correct, however, when we utilize progressive groups of three points, equally spaced in time, and compute the value toward which the temperature converges. Employing equally spaced points at later times, higher values for the equilibrium temperature are computed. It is clear that ϱ of eqn. 1 is too small. The departure of the experimental curve, Fig. 3, from the simple exponential form is also conspicuous in the first parts of the recovery. Two modifications in eqn. 1 are indicated, therefore:

(a) It is reasonable that recovery from supercooling should be governed primarily by energy rather than force considerations. In such case, it is more reasonable that it be 2 than 1.

(b) The superficial resemblance of the recovery curve to exponential appears to be caused by the effect of increase in total crystal area which has its greatest effect during the early part of the recovery from supercooling.

It is necessary, therefore, to include a modification that depends on the increase in total surface.

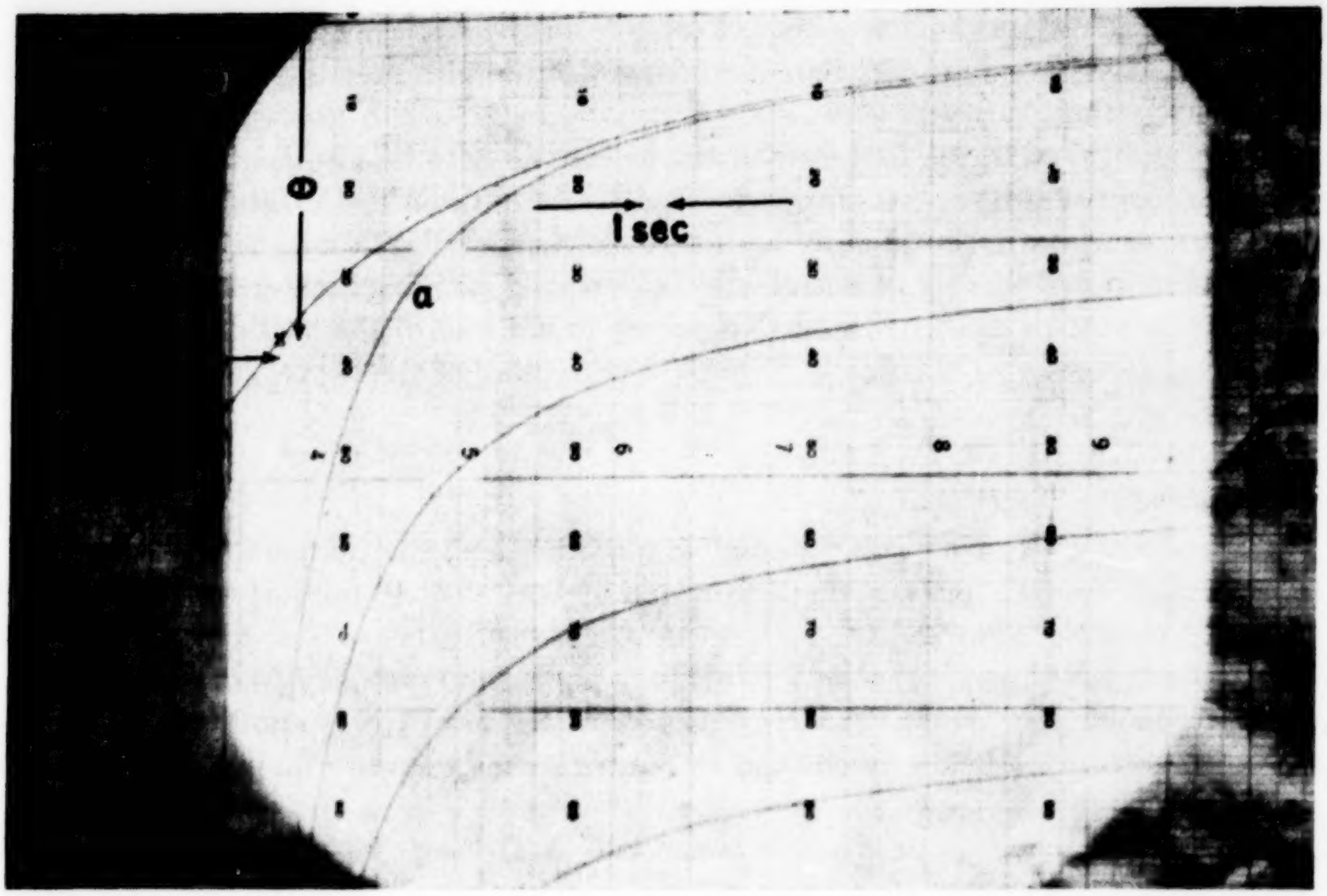

Fig. 3. Recovery from supercooling. Smooth line running through Θ_b, the time and temperature of nucleation and Θ, any subsequent condition, is the instrumental plot of recovery. The equilateral hyperbola (a) is so projected that it gradually converges with the recovery curve as time advances. It should be borne in mind that Θ corresponds to the amount by which the temperature is below equilibrium temperature at that time and not below any fixed temperature. The interval between fine vertical lines is 1 sec.

Microscopical examinations of samples that have recovered from supercooling during stirring show the crystals to be nearly of one size. This indicates that all or nearly all crystal nuclei form very early in the recovery processes. In such case, the crystalline surface at any time will be proportional to the two-thirds power of the change from the amount of supercooling $\Theta_\circ$ that prevailed when nucleation occurred. Two reasonable changes can be introduced into our original presumption, giving us

$$\frac{d\Theta}{dt} = -n(\Theta_\circ - \Theta)^{\frac{2}{3}}\,\Theta^2 \qquad (2)$$

Integration of this yields an awkward expression[*] that does not provide a simple correction of temperature for the lingering effects of supercooling. It is evident, however, that the effects of increasing surface become less significant as the surface becomes larger. As Θ becomes small in relation to $\Theta_\circ$, the term $(\Theta_\circ - \Theta)$ becomes more

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[*] $$-nt = \int^{\Theta} \frac{d\Theta}{\Theta^2(\Theta_\circ - \Theta)^{\frac{2}{3}}} = -\frac{(\Theta_\circ - \Theta)^{\frac{1}{3}}}{\Theta_\circ \Theta} + \frac{2}{3\Theta_\circ^{\frac{5}{3}}} \left[\frac{1}{2}\log\left(\frac{\left\{(\Theta_\circ - \Theta)^{\frac{1}{3}} - \Theta_\circ^{\frac{1}{3}}\right\}}{(\Theta_\circ - \Theta)^{\frac{2}{3}} + \Theta_\circ^{\frac{1}{3}} + \Theta_\circ^{\frac{2}{3}}}\right) + \right.$$
$$\left. + \sqrt{3}\arctan\left(-\frac{2(\Theta_\circ - \Theta)^{\frac{1}{3}} + \Theta_\circ^{\frac{1}{3}}}{\sqrt{3}\,\Theta^{\frac{1}{3}}}\right)\right] + C$$

nearly constant and the differential for an important part of the recovery period approaches the form

$$-n\mathrm{d}t = \frac{\mathrm{d}\Theta}{\Theta^2} \quad \ldots\ldots\ldots\ldots \quad (3)$$

This of course integrates to

$$nt = \frac{1}{\Theta} + C$$

where C establishes the time coordinates, Θ is the amount by which temperature at any moment is below equilibrium, and n a constant involving many rate elements. This equation is obviously that of an equilateral hyperbola.

We are again able to use the projective method. Curve *a* of Fig. 3 is the photographic record of an equilateral hyperbola projected upon the machine plot of a recovery from supercooling and adjusted for scale and for horizontal and vertical position in relation to the coordinates. It is adjusted so that it lies below the recovery curve in the first part of the recovery where increase of crystalline area is important and converges with the data after 15 or 20 seconds when the changing size becomes less important. From this placement, the constant n and the reference temperature from which Θ is measured can be evaluated, and the amounts by which the effects of supercooling lingered in the data of Fig. 2 can be computed. In Fig. 4, which shows the uncorrected

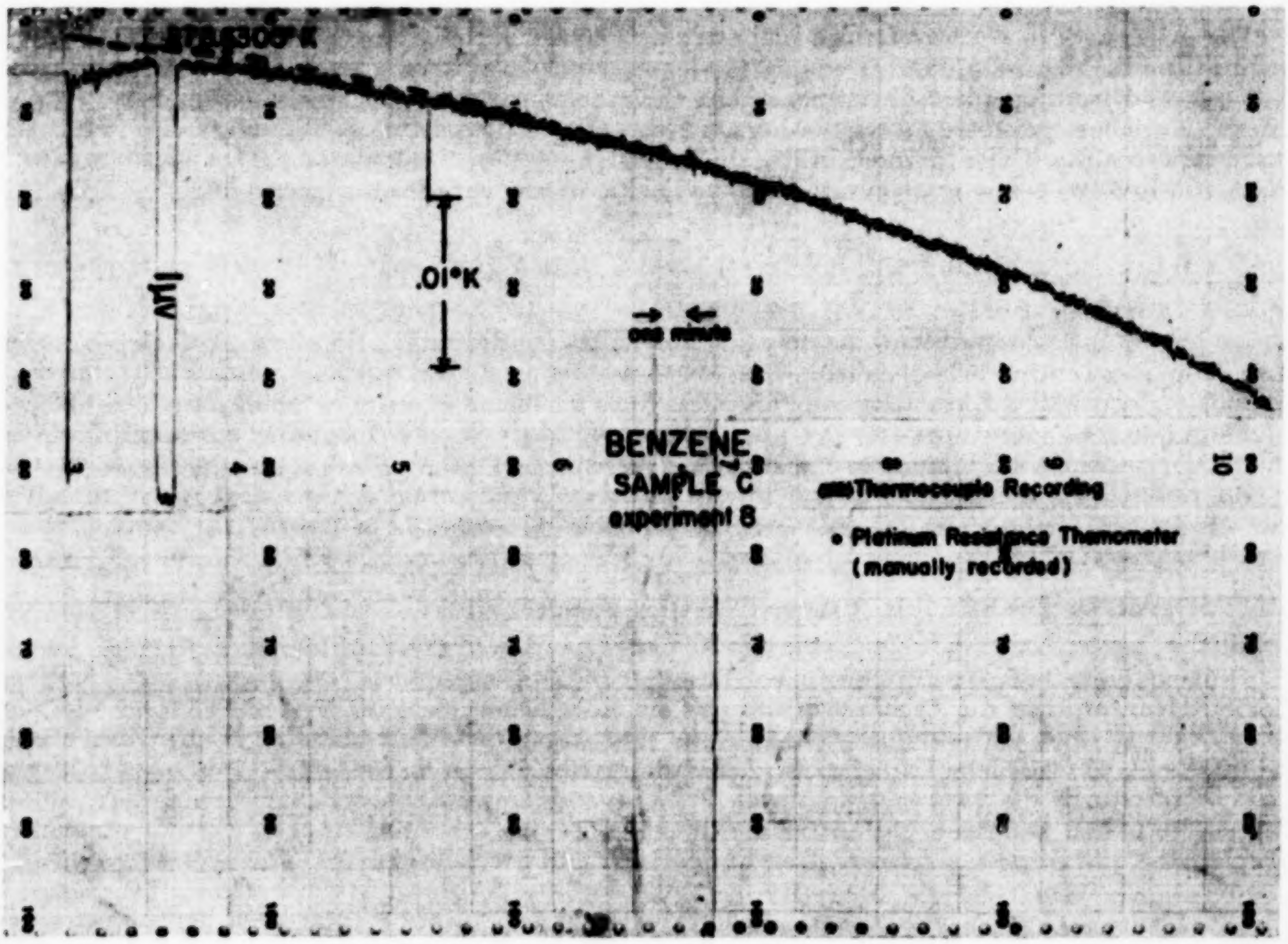

Fig. 4. Correction for effects of supercooling. The waving curve represents the same recorded thermocouple plot as in Fig. 2, simultaneous point determinations with a platinum resistance thermometer being superimposed as circles. Corrections for supercooling were based upon the evidence in Fig. 3 and are here plotted as dashes. On this basis it would appear that significant failure to recover from supercooling extends much longer than has usually been inferred.

data of Fig. 2 as a solid line, corrections to obviate the effects of supercooling have been introduced as circles. This corrected curve can be used for a more exact and more confident judgment of the values of both the triple point of the ideally pure material and of the material as contaminated by soluble impurities.

By correcting the data of a cryoscopic run for the effects of supercooling and subjecting the results to fit against a computed curve corresponding to the theoretical depression of temperature as a function of time, several advantages are obtained. On the basis of experiments which are still limited, it appears that the dependence of the calculated freezing point of the theoretically pure substance upon the amount of contaminant is practically if not entirely eliminated. Within the various uncertainties, it corresponds to the value found by ordinary procedures when exceptionally pure substances are employed. Likewise, the uncertainty in the evaluation of the temperature of first freezing of an actual sample, based upon the personal selection of the portion of a cooling curve that is assumed to be "good," largely disappears.

All work in this paper is based upon freezing curves and curves of the recovery from supercooling that were made by GAYLON S. ROSS, to whom I am deeply grateful.

SUMMARY

The accuracies of determinations of purity and freezing point based upon cryometric freezes suffer from the scatter of data, from the failure of systems ever to recover from the effects of supercooling, and from complex phenomena that elevate temperature during the later parts of runs. Methods are here proposed for decreasing the errors caused by scatter of data and failure to recover from supercooling. These methods utilize the optical projection of calculated curves upon the actual data and involve a new interpretation of the nature of recovery from supercooling.

RÉSUMÉ

La précision des déterminations de pureté et de points de congélation basées sur des mesures cryoscopiques souffre de la dispersion des résultats obtenus, du fait que les systèmes ne recouvrent jamais l'état primitif après avoir subi les effets de la surfusion et enfin de phénomènes complexes qui font que la température s'élève vers la fin des expériences. Dans ce mémoire l'auteur propose des méthodes destinées à diminuer les erreurs dues à la dispersion des résultats et au manque de rétablir l'état primitif après surfusion. Ces méthodes utilisent la projection optique des courbes calculées sur les données obtenues et causent une interprétation nouvelle de la nature du rétablissement après surfusion.

ZUSAMMENFASSUNG

Die Genauigkeit der Bestimmungen von Reinheit und Gefrierpunkt auf kryometrischer Grundlage leidet darunter, dass die Ergebnisse weit aus einander liegen, dass die Systeme sich nie von den Auswirkungen der Unterkühlung erholen und dass komplizierte Erscheinungen die Temperatur gegen Ende der Versuche erhöhen. In der vorliegenden Arbeit werden Methoden vorgeschlagen welche die durch die zwei erstgenannten Fehlerquellen verursachten Fehler vermindern sollen. Diese Methoden benutzen die optische Projektion der berechneten Kurven auf die wirklichen Ergebnisse und bringen eine neue Auslegung der Wiederherstellung nach Unterkühlung mit sich.

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AUSWERTUNG VON ERSTARRUNGS- UND SCHMELZKURVEN ZUR BERECHNUNG DES REINHEITSGRADES MITTELS MASCHINENLOCHKARTEN

von

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Die zeitabhängige Funktion der Erstarrungs- oder Schmelztemperatur eines Zweiphasensystems flüssig-fest lässt sich für ein thermodynamisches Phasengleichgewicht theoretisch erfassen. Ausgehend vom Raoultschen Gesetz und unter der Annahme, dass die Kristallisations- bzw. Aufschmelzgeschwindigkeit zeitkonstant ist, ergibt sich für den Temperaturverlauf des Erstarrungs- bzw. Schmelzvorganges eine Exponentialfunktion, die sich angenähert und für den praktischen Gebrauch ausreichend durch eine Hyperbelfunktion

$$T = T_F - \frac{b}{1 - cZ} \tag{1}$$

wiedergeben lässt*. Hierbei sind T und Z die Variablen der Temperatur und der Zeit, T_F ist die Erstarrungstemperatur der vollkommen reinen Substanz, b und c sind Konstanten, die die Form der Hyperbel bestimmen. Für $Z = 0$ stellt T_0 die Temperatur dar, bei der für eine vorliegende Substanz der erste bzw. letzte Kristallkeim im Gleichgewicht mit der flüssigen Phase steht.

Die Temperatur-Zeit-Kurven werden mit einer besonderen Registriereinrichtung aufgeschrieben; dafür erfolgt die Temperaturmessung mit Platinwiderstandsthermometern**, die im Messbereich von — 190°C bis + 150°C mit einem Streubereich von etwa ± 0.01°C absolute Werte liefern. Der Widerstand der Thermometer wird für die Temperaturmessung mit einer besonderen Wheatstoneschen Brückenschaltung gemessen, bei der die Widerstände in den Brückenzweigen einer Präzisionskurbelmessbrücke in Stufen von 0,1 Ohm abgeglichen werden. Der Brückenstrom und damit auch der über das Thermometer fliessende Strom wird dadurch unabhängig von dem Widerstandswert des Thermometers. Als Stromquelle für die Brücke dient ein

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* Vgl. W. P. WHITE, *J. phys. Chem.*, 24 (1920) 392; E. L. SKAU, *Proc. Am. Acad. Arts Sci.*, 67 (1933) 551; F. D. ROSSINI und Mitarb., *J. Research Natl. Bur. Standards*, 32 (1944) 197; H. KIENITZ in: HOUBEN-WEYL, *Methoden der organischen Chemie*, Bd. 2, G. Thieme, Stuttgart, 1954, S. 803-807.

** a: Widerstandsthermometer Leeds & Northrup, Philadelphia (Typ 8163; 25.5 Ohm [0°C]; geeicht v. National Bureau of Standards, Washington, zwischen —190°C und 500°C). b: Widerstandsthermometer in Sonderausführung W. C. Heraeus, Hanau (Typ 3/Q 3503; 100 Ohm [0°C]).

Spannungskonstanthalter*, der eine Gleichspannung von 800 mV liefert. Zur Anzeige der Brückenasymmetrie wird anstelle des sonst üblichen Spiegelgalvanometers für die Registrierung der Temperatur-Zeit-Kurven ein lichtelektrischer Verstärker** mit anschliessend angeschaltetem Tintenschreiber verwendet. Die Empfindlichkeit der Messanlage wird so eingestellt, daß eine Brückenasymmetrie von 0.1 Ohm einen Ausschlag des Tintenschreibers von 100 mm herbeiführt. Für das 25-Ohm-Thermometer beträgt demnach die Empfindlichkeit der Messanlage 0.01°C/mm Schreibbreite und für das 100-Ohm-Thermometer 0.0025°C /mm Schreibbreite***.

Es besteht nun die Aufgabe, aus den so registrierten Temperatur-Zeit-Kurven die Konstanten der Hyperbelfunktion zu bestimmen, um aus ihnen die Erstarrungstemperatur der vorliegenden Substanz und die Erstarrungstemperatur der völlig reinen Substanz zu berechnen. Geometrische (zeichnerische) und analytische (rechnerische) Methoden zu dieser Auswertung wurden — von drei Messpunkten ausgehend — von verschiedenen Autoren beschrieben****. Bei diesen Verfahren erweist es sich grundsätzlich als nachteilig, dass die richtige Auswahl von drei Bestimmungspunkten sehr schwierig ist und letztlich willkürlich bleibt und dass so für die Auswertung der gesamten Gleichgewichtskurve stets nur einzelne Punkte verwertet werden, während der gemessene Gesamtverlauf der Kurve nicht voll ausgenutzt wird. Es lag daher nahe, aus einer möglichst grossen Anzahl von Temperatur-Zeit-Wertepaaren der Erstarrungskurve die Konstanten T_F, b und c für die Hyperbel der allgemeinen Funktion

$$T = T_F - \frac{b}{1 - cZ} \tag{1}$$

zu suchen, die den gemessenen Kurvenverlauf am besten wiedergibt. Mit Hilfe der Ausgleichsrechnung läßt sich die vorliegende Aufgabe lösen. Nach ihr seien für die anzunähernde Funktion $y = f(x, a_1, a_2, a_3)$ eine Anzahl n Funktionswerte y_i; x_i gegeben. a_1, a_2 und a_3 seien die gesuchten Parameter der anzunähernden Funktion. Dazu wird gefordert, daß die Summe der Quadrate der Abweichungen sämtlicher Ordinaten y_i zum Minimum wird:

$$Q = \sum_{i=1}^{n} (v_i)^2 = \sum_{i=1}^{n} (y - y_i)^2 = \text{Min} \tag{2}$$

Diese Bedingung ist für ein Verschwinden der partiellen Ableitungen erfüllt:

$$\frac{\partial Q}{\partial a_j} = 0 \qquad (j = 0, 1, 2) \tag{3}$$

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* Siemens und Halske, Karlsruhe, üblicherweise in dem Kompensationsregler eingebaut.

** Siemens und Halske, Karlsruhe, lichtelektrischer Verstärker mit spannungsempfindlicher Kompensationsschaltung, Eingangsempfindlichkeit 175 mV bei 87 Ohm Eingangswiderstand.

*** Da die Reproduzierbarkeitsgrenzen der Brückenwiderstände einen Fehler der Temperaturmessung von etwa ± 0.01°C absolut bedingen, kann die hohe Registrierempfindlichkeit für das 100-Ohm-Thermometer nur zur Erhöhung der Relativgenauigkeit in einem engen Messbereich ausgenutzt werden.

**** A. R. Glasgow, A. J. Streiff und F. D. Rossini, *J. Research Natl. Bur. Standards*, 35 (1945) 355; H. Kienitz, loc. cit., S. 812-814.

Im hier vorliegenden Fall der Berechnung eines Hyperbeltrends nach der Ausgleichsrechnung ist von der Hyperbelfunktion (1) auszugehen, in der zur Vereinfachung und Übersichtlichkeit $T_F = a$, $T = y$ und $Z = x$ gesetzt werden:

$$y = a - \frac{b}{1 - cx} \tag{4}$$

Die anzunähernde Funktion (4) hat also die Parameter a, b und c. Da sich Q, nach (2) unter Verwendung von (4) berechnet, nur sehr umständlich nach den Parametern partiell ableiten und auflösen lässt, wird die Funktion (4) zunächst in folgender Weise umgewandelt:

$$(y - a)\,(1 - cx) + b = 0 \tag{5}$$

Die Abweichung v_i für den Messpunkt y_i; x_i ist dann*

$$v_i = (y_i - a)\,(1 - cx_i) + b \tag{6}$$

und die Summe der Fehlerquadrate soll sein

$$Q\,(a, b, c) = \sum_{i=1}^{n} (v_i)^2 = \sum_{i=1}^{n} \left\{(y_i - a)\,(1 - cx_i) + b\right\}^2 = \text{Min} \tag{7}$$

Vom Ausdruck (7) lassen sich die partiellen Ableitungen bilden

$$\frac{\delta Q}{\delta a} = Q_a' = 2 \sum_{i=1}^{n} \left\{(y_i - a)\,(1 - cx_i) + b\right\}(1 - cx_i) = 0 \tag{8}$$

$$\frac{\delta Q}{\delta b} = Q_b' = 2 \sum_{i=1}^{n} \left\{(y_i - a)\,(1 - cx_i) + b\right\} = 0 \tag{9}$$

$$\frac{\delta Q}{\delta c} = Q_c' = 2 \sum_{i=1}^{n} \left\{(y_i - a)\,(1 - cx_i) + b\right\} x_i\,(a - y_i) = 0 \tag{10}$$

Für die Berechnung von a, b und c ergeben sich die Bestimmungsgleichungen:

$$\sum_{i=1}^{n} \left\{(y_i - a)\,(1 - cx_i)^2\right\} + nb - bc \sum_{i=1}^{n} x_i = 0 \tag{11}$$

$$\sum_{i=1}^{n} \left\{(y_i - a)\,(1 - cx_i)\right\} + nb = 0 \tag{12}$$

$$\sum_{i=1}^{n} \left\{(y_i - a)^2\,(cx_i^2 - x_i)\right\} + ab \sum_{i=1}^{n} x_i - b \sum_{i=1}^{n} x_i y_i = 0 \tag{13}$$

Gleichung (12) nach b aufgelöst

$$b = a - \frac{1}{n} \Sigma y_i + \frac{c}{n} \Sigma x_i y_i - \frac{ac}{n} \Sigma x_i \tag{14}$$

wird in (11) eingesetzt:

$$c\left\{\Sigma x_i^2 y_i - \frac{\Sigma x_i \Sigma x_i y_i}{n}\right\} - ac\left\{\Sigma x_i^2 - \frac{\Sigma x_i \Sigma x_i}{n}\right\} - \left\{\Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{n}\right\} = 0 \tag{15}$$

$$cB - acC - A = 0 \tag{16}$$

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* Die v_i nach (2) und (6) sind streng genommen nicht gleich definiert. Wie jedoch leicht zu zeigen ist, spielt der Unterschied für die folgende Ableitung keine Rolle.

sowie in (13) eingesetzt:

$$(17)\quad a^2c\left\{\Sigma x_i^2 - \frac{\Sigma x_i \Sigma x_i}{n}\right\} - 2ac\left\{\Sigma x_i^2 y_i - \frac{\Sigma x_i \Sigma x_i y_i}{n}\right\} + a\left\{\Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{n}\right\}$$
$$+ c\left\{\Sigma x_i^2 y_i^2 - \frac{\Sigma x_i y_i \Sigma x_i y_i}{n}\right\} - \left\{\Sigma x_i y_i^2 - \frac{\Sigma x_i y_i \Sigma y_i}{n}\right\} = 0$$

$$(18)\quad a^2c\ C - 2ac\ B + a\ A + c\ E - D = 0$$

Aus den Gleichungen (12), (16) und (18) können nun die Parameter *a*, *b* und *c* errechnet werden

$$(19)\quad a = \frac{AE - BD}{AB - CD}$$

$$(20)\quad b = a - \frac{1}{n}\Sigma y_i + \frac{c}{n}\Sigma x_i y_i - \frac{ac}{n}\Sigma x_i$$

$$(21)\quad c = \frac{AB - CD}{B^2 - CE}$$

wobei zur Vereinfachung die Hilfsgrössen *A*, *B*, *C*, *D* und *E* eingeführt werden:

$$(22)\quad A = \Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{n}$$

$$(23)\quad B = \Sigma x_i^2 y_i - \frac{\Sigma x_i y_i \Sigma x_i}{n}$$

$$(24)\quad C = \Sigma x_i^2 - \frac{\Sigma x_i \Sigma x_i}{n}$$

$$(25)\quad D = \Sigma x_i y_i^2 - \frac{\Sigma x_i y_i \Sigma y_i}{n}$$

$$(26)\quad E = \Sigma x_i^2 y_i^2 - \frac{\Sigma x_i y_i \Sigma x_i y_i}{n}$$

Die numerische Rechnung des Hyperbeltrends aus einer gemessenen Erstarrungskurve erfolgt nun in der Weise, dass ausgehend von beispielsweise zehn Messwerten, deren zeitliche Abstände nicht gleich zu sein brauchen, zunächst unter Verwendung der Ausdrücke:

$$(27)\quad \Sigma Z_i = \Sigma x_i;\ \Sigma T_i = \Sigma y_i;\ \Sigma Z_i T_i = \Sigma x_i y_i;\ \Sigma Z_i^2 = \Sigma x_i^2;\ \Sigma T_i^2 = \Sigma y_i^2;\ \Sigma Z_i^2 T_i = \Sigma x_i^2 y_i;$$
$$\Sigma Z_i T_i^2 = \Sigma x_i y_i^2;\ \Sigma Z_i^2 T_i^2 = \Sigma x_i^2 y_i^2$$

die Hilfsgrössen *A*, *B*, *C*, *D* und *E* nach (22) bis (26) errechnet werden und aus diesen dann die Parameter *a*, *b* und *c* der Hyperbel. Da die immer gleichartige Rechnung sehr langwierig ist, wird sie mit Hilfe von Maschinenlochkarten auf einem Elektronenrechner (Bull Gamma 3) mit angeschlossener Tabelliermaschine (Bull) in der Weise durchgeführt, dass auf den einzelnen Lochkarten eines Lochkartensatzes die gleichbleibende Probennummer und das Zeit-Temperatur-Wertepaar eingelocht sind. Die Auswertung von Erstarrungs- und auch von Schmelzkurven kann mit dieser Rechenhilfe für die Bestimmung des Reinheitsgrades routinemässig erfolgen. Man erhält so nicht nur die ausgeglichenen Parameter der Hyperbelfunktion des Erstarrungs- bzw. Schmelzvorganges, sondern kann in einfacher Weise auch die Standardabweichung für die gemessene Kurve von der theoretisch geforderten errechnen. Sie gibt eine

Kontrolle, ob die gemessene Kurve im ganzen oder in Teilen tatsächlich den Forderungen nach Phasengleichgewicht während des Erstarrungs- bzw. Schmelzvorganges sowie nach Konstanz der Kristallisations- bzw. Aufschmelzgeschwindigkeit entspricht.

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ZUSAMMENFASSUNG

Die zeitabhängige Funktion der Erstarrungs- bzw. Schmelztemperatur eines Zweiphasensystems flüssig-fest ist unter der Annahme thermischen Gleichgewichtes und konstanten Wärmeentzuges des Systems oder konstanter Wärmezufuhr (konstante Kristallisations- bzw. Aufschmelzgeschwindigkeit) näherungsweise eine Hyperbel. Die Temperatur-Zeit-Kurven werden mit Hilfe einer besonderen Messapparatur registriert. Für die Auswertung dieser Kurven besteht die Aufgabe: 1. die Erstarrungstemperatur einer vorliegenden Substanz zu bestimmen, bei der gerade der erste (oder letzte) Kristallkeim im Gleichgewicht mit der flüssigen Phase steht, 2. die extrapolierte Erstarrungstemperatur der völlig reinen Substanz zu ermitteln und 3. zu kontrollieren, ob die gemessene Kurve tatsächlich dem Phasengleichgewicht entspricht. Dazu wird mit Hilfe der Ausgleichsrechnung zu beispielsweise zehn Wertepaaren der Temperatur und der Zeit die Hyperbel der allgemeinen Funktion

$$T = T_F - \frac{b}{1 - cZ}$$

gesucht, die den gemessenen Kurvenverlauf am besten wiedergibt, d.h. für die die Summe der Quadrate der Abweichungen von den gemessenen Temperaturen zu den aus der Hyperbelfunktion errechneten ein Minimum darstellt. Man erhält so weit besser als mit der analytischen oder geometrischen Methode der Auswertung über drei Messpunkte der Gleichgewichtskurve den Erstarrungspunkt einer vorliegenden Substanz sowie zusätzlich die Standardabweichung der gemessenen Kurve von der theoretisch geforderten Hyperbel. Da die numerische Berechnung eines Hyperbeltrends recht zeitraubend ist, wird sie mit Hilfe von Maschinenlochkarten auf einem Elektronenrechner durchgeführt. Die Bestimmung des Reinheitsgrades von Substanzen kann auf diese Weise routinemässig erfolgen.

SUMMARY

Assuming thermal equilibrium and constant heat withdrawal from the system or constant heat supply (constant rate of crystallization or melting), the time-dependent function of the freezing or melting point of a two-phase liquid-solid system is approximately a hyperbola. The time-temperature curves were recorded with the help of a special measuring apparatus. In order to evaluate these curves it is necessary: (1) to determine the freezing point of a given substance, at which the first (or last) crystal nucleus is exactly in equilibrium with the liquid phase, (2) to ascertain the extrapolated freezing point of the completely pure substance, and (3) to check whether the measured curve really corresponds to the phase equilibrium. One searches for, for example, ten pairs of values of temperature and time, the hyperbola of the general function

$$T = T_F - \frac{b}{1 - cZ}$$

that best renders the measured course of the curve, *i.e.* the one that makes the sum of the squares of the deviations of the measured temperatures from that calculated from the hyperbola function a minimum. In this way, the freezing point of a given substance, as well as the standard deviation of the measured curve from the hyperbola is better obtained than with the analytical or geometrical methods of evaluating via 3 points on the equilibrium curve. Since the numerical calculation of a hyperbola trend is very time-consuming, it is accomplished with the help of machine punch-cards in an electronic computer. The determination of the degree of purity of substances can be routinely carried out in this way.

RÉSUMÉ

En admettant qu'il y a équilibre thermique et que les pertes ou les gains de chaleur du système sont constants (vitesse de cristallisation ou de fusion constante), la courbe en fonction du temps de la température de solidification ou de fusion d'un système à deux phases liquide-solide est approximativement une hyperbole. Les courbes température-temps sont enregistrées à l'aide d'un appareil de mesure spécial. Pour l'évaluation de ces courbes il faut: 1° déterminer la température de solidification d'une substance donnée pour laquelle le premier (ou dernier) cristal est justement en équilibre avec la phase liquide, 2° trouver la température de solidification extrapolée de la substance absolument pure et 3° contrôler si la courbe mesurée correspond réellement à l'équilibre des phases. A cet effet on cherche, par exemple pour dix paires de valeurs de la température et du temps, l'hyperbole de la fonction générale

$$T = T_F - \frac{b}{1 - cZ}$$

qui rend le meilleur compte de la courbe mesurée, c'est à dire pour laquelle la somme des carrés des déviations entre les températures mesurées et celles calculées à la base de la fonction hyperbolique est minimum. L'on obtient ainsi, bien mieux que par les méthodes d'évaluation analytique et géometrique par trois points de la courbe d'équilibre, le point de solidification de la substance donnée et, de plus, la déviation standard entre la courbe mesurée et l'hyperbole théorique. Comme le calcul numérique du cours d'une hyperbole prend beaucoup de temps, on l'exécute à l'aide de fiches perforées sur une machine à calculer électronique. L'on peut ainsi déterminer le degré de pureté d'une substance d'une manière routinière.

Eingegangen den 23. April 1957

DIE ERLANGUNGSFÄHIGKEIT DES GLEICHGEWICHTES IN SYSTEMEN, DIE AUS FLÜSSIGKEIT UND WENIGSTENS AUS EINER FESTEN PHASE GEBILDET SIND

von

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Es sind drei allgemeine Methoden der Bestimmung von Erstarrungstemperaturen bekannt und zwar: die kinetische, die kalorimetrische und die statische Methode. Die erste, nämlich die kinetische Methode, beruht auf der Messung der Temperatur eines Systems bestehend aus Flüssigkeit und fester Phase, zu welchem Wärme zugeführt oder von welchem Wärme in gleichmässiger Weise abgeführt wird. Die Untersuchung der erlangten Erstarrungs- und Schmelzpunktkurven führt zur Feststellung der Erstarrungstemperatur einer hundertprozentig reinen Substanz und des Reinheitsgrades der Probe. Bei der kinetischen Methode untersucht man in der Regel Proben, die mit wasser- und kohlendioxydfreier Luft gesättigt sind. Bei der kalorimetrischen Methode benutzt man das adiabatische Kalorimeter. Durch das Zuführen einer bestimmten Energiemenge zum System fest-flüssig bestimmt man jedesmal das sich einstellende Temperatur-Gleichgewicht. Die Feststellung einer Reihe von Punkten des Gleichgewichtes ermöglicht die Bestimmung der Erstarrungstemperatur und des Reinheitsgrades einer Substanz. Bei der statischen, dilatometrischen Methode wird ebenfalls eine Reihe von Gleichgewichtspunkten bei verschiedenen Erstarrungsgraden der Probe bestimmt. Man misst hier die Änderung des Volumens des Systems deren Funktion die Gleichgewichtstemperatur ist. Bei dieser Methode ist es besonders leicht die Gleichgewichtstemperaturen von Proben, die keine Luftbestandteile enthalten, zu messen und den Tripelpunkt der Substanz zu bestimmen.

Aus obigem folgt, dass während die erstgenannte Methode der Untersuchung von Gleichgewichten fest-flüssig typisch kinetisch ist, die beiden übrigen, nämlich die kalorimetrische und die das dilatometrische Kryometer benutzende Methode, typisch statische Methoden sind, die die Feststellung der thermodynamischen Gleichgewichtszustände bezwecken. Aus praktischen Gründen findet die kinetische Methode heute öftere Anwendung zur Bestimmung des Reinheitsgrades von Substanzen. Es entsteht jedoch in jedem einzelnen Falle die Grundfrage, wie weit die durch sie erlangten Ergebnisse genau, glaubwürdig und mit den mittels der übrigen zwei Methoden erreichten Ergebnissen vergleichbar sind. Der Wert der gemessenen Gleichgewichtstemperaturen, die mittels der kinetischen Methode bestimmt wurden, kann von dem wirklichen Wert in dem Falle abweichen, wenn die Kristallisations- oder Schmelzgeschwindigkeit zur Erreichung des jeweiligen Gleichgewichtszustandes fest-flüssig nicht genügend gross ist.

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Unlängst erschien eine Monographie von MATHIEU[1], welcher systematische Untersuchungen von acht Substanzen, die im Zustande weitgehenden Reinheitsgrades waren, ausgeführt hat; er bestimmte ihre Erstarrungspunkte als auch die Tripelpunkte, wobei er sich der kinetischen und der Methode des dilatometrischen Kryometers bediente. In unserem Institute wurden zahlreiche kryometrische Messungen an Substanzen von hohem Reinheitsgrad ausgeführt, wobei zwei Typen von Kryometern, das dilatometrische und das Differentialkryometer angewendet wurden[2,3]. Es wurden die Erstarrungs- und Tripelpunkte von Benzol-, Naphtalin- und 2-Methylnaphtalinproben bestimmt. Was das Benzol anbelangt, so wurden nach Kalibrierung des Widerstandsthermometers Resultate, die mit den jenigen von MATHIEU zusammenstimmen, erreicht.

In der oben zitierten Arbeit gibt MATHIEU an, dass er gleiche Werte für einige Substanzen mittels beider genannter Methoden d.h. der kinetischen und des Dilatometers-Kryometers erlangt hat. Das bedeutet aber nicht, dass man bei anderen Substanzen regelrechte Resultate erreichen kann, besonders bei jenen, deren Schmelz- oder Kristallisationsgeschwindigkeit zu klein ist und deshalb eine Unterkühlung oder Überhitzung des untersuchten Systems erfolgt. Aus der Veröffentlichung von MATHIEU ersieht man klar, dass er auf Schwierigkeiten stiess, wenn Substanzen untersucht wurden, deren Kristallisation zu langsam verläuft; zu solchen Substanzen gehören: Benzophenon, Salol u. dgl. Ausserdem hat MATHIEU, dessen Ziel es war einige Substanzen als thermometrische Standards vorzuschlagen, im voraus manche Substanzen, die sich nicht mittels der kinetischen Methode untersuchen liessen und auch die, welche grosse Schwierigkeiten bei ihrer Reinigung verursachten, von den Untersuchungen ausgeschlossen. Es soll hier erwähnt werden, dass ein typisches Beispiel einer praktisch nicht kristallisierenden Substanz auch bei tiefer Unterkühlung, das Glyzerin ist; es sei ferner erwähnt, dass die Isomeren des Äthylnaphtalins eine längere Zeit und eine tiefe Temperatur zur Kristallisation brauchen.

Das wichtigste Problem bei Erstarrungstemperaturmessungen ist, ob überhaupt das thermodynamische Gleichgewicht in dem System erreichbar sei. Die Fähigkeit des Systems das thermodynamische Gleichgewicht zu erlangen, können wir als sog. "thermische Empfindlichkeit" bezeichnen.

Die Untersuchung der thermischen Empfindlichkeit eines Systems hat zum Zwecke die Feststellung, dass die dem System gelieferte oder von ihm abgeführte Wärmemenge quantitativ zur Phasenumwandlung verwendet wird; im Falle der statischen oder kalorimetrischen Methode aber, in welchem Grade das System auf schwache Überhitzung oder Unterkühlung reagiert.

Unabhängig von den allgemein bekannten Kriterien des Gleichgewichtes, die bei der Analyse der Erwärmungs- und Abkühlungs-Kurven, die nach der kinetischen Methode erlangt wurden, angewendet werden, wäre es von Nutzen für langsam kristallisierende Substanzen die Grenzgeschwindigkeit des Wärmeaustausches, bei welcher die Kurve noch den Gleichgewichtstemperaturen entspricht, zu bestimmen. Man könnte diese Geschwindigkeit als Mass der thermischen Empfindlichkeit der untersuchten Substanz in Bezug auf die standarisierten Bedingungen der Durchführung der Messungen bezeichnen.

Im Falle statischer Methoden kann die Untersuchung der thermischen Empfindlichkeit auf der Zuführung zu oder Wegnahme von dem System kleiner Wärmemengen bestehen, d.h. solcher, die in den Grenzen der Genauigkeit der angewandten Methode,

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die Gleichgewichtstemperatur nicht ändern sollen. Ferner soll festgestellt werden, nach welcher Zeit die Temperatur zu dem Stand zurückkehrt, der dem bestimmten Verhältnis der festen und flüssigen Phase entspricht und welcher Unterkühlung bzw. Unterhitzung das System unter den gegebenen Versuchsbedingungen unterliegt.

Wir untersuchten die thermische Empfindlichkeit der Systeme mit Anwendung der Methode des dilatometrischen Kryometers. Der Versuch beruhte darauf, dass man ins Innere des Systems, in welchem sich eine bestimmte Temperatur eingestellt hat und sich eine hinreichend lange Zeit z.B. 20 bis 40 Minuten erhalten hat, eine recht kleine Wärmemenge in der Grösse von 0.2 bis 0.5 Kalorien eingeführt hat. Zu diesem Zwecke wurde das Thermometer aus der Thermometerhülse des Kryometers herausgenommen und um eine bis zwei Zehntel Celsiusgrade erwärmt. Nachher wurde das Thermometer wieder in die Thermometerhülse des Kryometers eingeführt. Es wurde die Zeit gemessen, nach welcher das System wieder das thermodynamische Gleichgewicht erreicht hat. Da die Wärmemenge, die dem System zugeführt wurde, im Verhältnis zu der Schmelzwärme der Substanz klein war, so müsste auch die Menge der geschmolzenen Kristalle sehr klein sein. Die Konzentration der Verunreinigungen in der Lösung ist praktisch unverändert geblieben. Deshalb sollte das System die Gleichgewichtstemperatur, die vor dem Wärmezufluss herrschte, wieder erreichen. Wenn mit Benzolproben hohen Reinheitsgrades gearbeitet wurde, konnte die Anfangstemperatur schon nach 15 bis 20 Minuten hergestellt werden. Im Falle eines Benzols, dass mehr Verunreinigungen enthält (sog. Nitrationsbenzol) wurde das Temperaturniveau um einige Tausendstel Grade höher oder niedriger im Verhältnis zu der vorigen erreicht.

Dies kann als ein Zeichen dafür gelten, dass die thermische Empfindlichkeit des Systems im Falle des Benzols verhältnismässig gross ist. Auf diese Weise ist es verständlich, das die Erstarrungstemperaturen, welche auf zwei verschiedenen Wegen (d.h. mittels der kinetischen und der statischen Methode durch MATHIEU, als auch mittels der statischen durch uns) erzielt wurde, übereinstimmen. Im Falle des chemisch reinen 2-Methylnaphtalins lag die thermische Empfindlichkeit in befriedigend engen Grenzen ± 0.002°C. Jedoch wurde bei den Proben, die mehr verunreinigt waren, die Temperaturschwankungen in den Grenzen bis 0.010°C gefunden.

Um die thermische Empfindlichkeit eines Systems fest-flüssig zu prüfen, wurden einige eutektische Systeme, die aus Wasser und ziemlich schwer löslichen (in der Nähe von 0°C) anorganischen Salzen gebildet sind, Untersuchungen unterzogen. Es wurde z.B. das System Kaliumbichromat-Wasser durch J. SWIETOSLAWSKA untersucht; die untersuchte eutektische Mischung war praktisch vollkommen rein. Ein Beweis dafür ist, dass die Erstarrungstemperaturkurve für verschiedene Prozentgehalte der festen Phase eine Gerade und zur L-Achse Parallele auf dem L,T-Diagramm war. Trotzdem konnte der stabile Zustand nicht so schnell erreicht werden. Erst nach wiederholten Zu- und Abführen kleiner Wärmemengen konnte jedenfalls die richtige Gleichgewichtstemperatur erreicht werden. Einer von uns (W. SWIETOSLAWSKI) untersuchte die eutektischen Mischungen, die aus Wasser und drei bis vier ziemlich schwerlöslichen Salzen bei 0°C gebildet waren. Obgleich in diesem Falle die eutektischen Mischungen "rein" waren, ein Zeichen dafür war der gerade Abschnitt der L,T-Kurve, kehrte das System nach Zuführen von kleinen Wärmemengen ins Anfangsstadium nicht zurück. Es wurden Temperaturschwankungen von 0.050°C beobachtet. Es muss angenommen werden, dass diese Temperaturschwankungen mit Bildung einiger und Auflösung von anderen Kristallen verbunden waren. Dabei hatte wahrscheinlich jedes der untersuchten anorganischen Salze seine spezifische Kristallisations- oder Auflösungsgeschwindigkeit.

Diese Versuche weisen deutlich darauf hin, dass sich das Gleichgewicht fest-flüssig nicht sofort einstellt, auch in solchen Systemen nicht, in denen die Kristallisationsgeschwindigkeit genügend gross und die Viskosität klein ist. Diese Erscheinung tritt mit besonderer Schärfe heraus, wenn mehr als eine feste Phase gebildet wird, z.B. im Falle der obengenannten polykomponenten eutektischen Systeme.

Daraus können folgende Schlussfolgerungen gezogen werden: jedesmal wenn die Erstarrungstemperatur oder der Reinheitsgrad der Substanz untersucht wird, soll die Probe der *thermischen Empfindlichkeit* des Systems vorgenommen werden, gleichgültig ob die statische oder die kinetische Methode angewendet wird. Es wäre vielleicht richtig den Experimentatoren zu empfehlen in jedem Falle die obengenannte thermische Empfindlichkeitsprobe des Systems durchzuführen.

Recommendations for preventing errors resulting from imperfect establishment of the phase equilibria, by W. SWIETOSLAWSKI, K. ZIEBORAK AND T. PLEBANSKI.

Investigations have been carried out by M. P. MATHIEU on the precise cryometric measurement of liquid-solid-gas equilibria of carefully purified individual substances. He established that proper and exact numerical data may be achieved by the kinetic, the adiabatic and the static methods (using dilatometric cryometers), provided that the velocity of crystallization or melting is sufficiently high to establish the real phase equilibria each time.

In order to test whether the velocity of formation or of melting of the solid phase is sufficiently high, it is recommended that the investigators should demonstrate in each case that this velocity is sufficient for the precise determination of the measured values.

The identity of the freezing and melting curves may be used for this purpose.

If the kinetic method is used, the change of solidification or melting velocity in both series of measurements should be applied in order to ensure that identical results are obtained.

If the adiabatic or the static method is used, the investigator should test, by introducing or by removing small amounts of heat, whether the phase equilibrium of the system examined is always completely restored.

It seems reasonable to call the methods mentioned above, the "thermal sensitivity test" of the systems examined.

In order to avoid the systematical errors often committed in the past it is important to note that a large number of substances exist which do not undergo crystallization, even in a supercooled state, and that the establishment of a phase equilibrium takes a long time. The glycerol and the two ethylnaphthalene isomers are typical examples: the first belongs to the substances undergoing extreme supercooling without crystallization, the second to the substances undergoing a slow crystallization in a very supercooled state.

For this reason additional measurements should be carried out each time so as to guarantee that the real phase equilibria were established in the systems examined.

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We would emphasise the importance of giving, for each individual substance, the triple point, and the solid-liquid phase equilibrium under the pressure of 1 atm of dry air (devoid of carbon dioxide).

The same suggestions apply to the thermal investigation of any kind of eutectic (and solid solution) equilibria.

SUMMARY

The difficulties associated with the precise determination of the freezing temperature of different systems containing one, two, or several solid phases are discussed. The "thermal sensitivity test" is suggested for testing whether the precision with which the thermodynamic liquid-solid phase equilibrium is restored is quite satisfactory.

The static method makes it possible to introduce or to remove very small quantities of heat and to observe whether or not the restoration of the phase equilibrium takes place. If a kinetic method is applied, the "thermal sensitivity" of the system may be tested by comparing the solidification and the melting curves determined at different crystallization or melting velocities.

RÉSUMÉ

Les auteurs discutent les difficultés inhérentes à la détermination précise de la température de congélation de différents systèmes contenants une, deux, ou plusieurs phases solides. Ils proposent le „test de sensibilité thermique" pour contrôler si la précision avec laquelle l'équilibre thermodynamique des phases liquide-solide est rétabli est bien satisfaisante.

La méthode statique permet d'introduire ou d'enlever de très petites quantités de chaleur et d'observer si le rétablissement de l'équilibre des phases a lieu. Si l'on emploie une méthode cinétique, on peut contrôler la „sensibilité thermique" du système en comparant les courbes de solidification et de fusion déterminées à différentes vitesses de cristallisation ou de fusion.

ZUSAMMENFASSUNG

Es werden die Schwierigkeiten erörtert, welche mit der genauen Bestimmung der Schmelztemperatur verschiedener Systeme die eine, zwei oder mehrere feste Phasen enthalten, verbunden sind. Der „thermische Empfindlichkeitstest" wird vorgeschlagen um zu prüfen, ob die Genauigkeit mit der das thermodynamische Gleichgewicht der flüssigen und festen Phasen wiederhergestellt wird, ganz befriedigend ist.

Die statische Methode ermöglicht es, sehr kleine Wärmemengen zu- oder abzuführen und zu beobachten, ob das Phasengleichgewicht sich wieder einstellt oder nicht. Wenn man eine kinetische Methode anwendet, kann die „thermische Empfindlichkeit" des Systems durch Vergleich der bei verschiedenen Kristallisations- und Schmelzgeschwindigkeiten bestimmten Kristallisations- und Schmelzkurven geprüft werden.

LITERATUR

[1] M. P. Mathieu, *Acad. roy. Belg., Classe sci. Mem.*, 28 (1953) 2.

[2] W. Swietoslawski, *Bull. intern. acad. polon. Sci., Ser. A*, (1948) 113-126; *J. Phys. Chem.*, 47 (1943) 590.

[3] W. Swietoslawski, *Metody rozdzielania i oczyszczania substancji*, PZWS, Warszawa, 1950.

[4] J. Scislowska-Swietoslawska, Vortrag an dem V. Kongress der Polnischen Chemischen Gesellschaft in Wroclaw, 1948; *Przeglad Chem.*, 6 (1948), No. 7-8, S. 12.

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COMPARISON OF CRYOSCOPIC DETERMINATIONS OF PURITY OF BENZENE BY THERMOMETRIC AND CALORIMETRIC PROCEDURES

by

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I. INTRODUCTION

For some time, workers at the National Bureau of Standards have been embarassingly aware of the discordant results sometimes yielded by the two methods upon which we principally depend to assay the purity of nearly pure compounds. Almost always the thermometric method, by which a stirred sample is frozen at nearly constant rate, had indicated larger impurity than the calorimetric method, by which an adiabatically controlled frozen sample is melted in stages by the addition of accurately controlled increments of energy. The fundamental physical principles and assumptions are the same in both cases, and the analysis depends upon the measurements of temperature. The discordances in assays by the two methods were dramatically laid bare when CINES[1] and MATHIEU[2] published comparisons of results obtained at the National Bureau of Standards using a thermometric method with those obtained at the U.S. Bureau of Mines employing the calorimetric procedure.

In general, we have tended to assume that the much more elaborate calorimetric method provides truer results, for reasons that do not need to be elaborated here. Neither method can be considered free of its own pitfalls, however, and it was decided to attempt a rigorous and objective comparison of the two methods. This depended on deliberate contaminations of an unusually pure sample, division of the contaminated samples in such manner that the compositions would not be altered, and independent determinations of purities by the two methods.

Fortunately for the independence of this comparison, the group at the National Bureau of Standards who use the calorimetric procedure work in a different building, in a different division, and under different supervisors from those who use the thermometric procedure. As a consequence, it was possible to plan a coordinated system of comparison in which each group of workers would be unaware of the results being achieved by the other and for both to be totally uninformed about the extent of the deliberate contaminations that had been made.

For the sake of objectivity, an elaborate scheme was employed so that no one could know the real measure of contamination until all results by both procedures had been reported. Thus the *n*-heptane with which a highly purified sample of benzene was to be contaminated was measured by three workers into 6 different weighed glass vessels. After they had been filled, the vessels were weighed by another worker who kept a private record of his results. Volumetric amounts of *n*-heptane were determined by still another participant. The vessels containing contaminant were entrusted to another worker, a young woman who did not otherwise participate in the study. When requested, she selected the sealed tubes of contaminant that were broken into the liquid benzene by another group of workers who alone knew the amount of the benzene to which the *n*-heptane was added. Only after all measurements and calculations had been completed were the scattered bits of information assembled from which it was possible to calculate the actual degree of contamination.

In the actual performance of analyses we felt that there was no reason to use any techniques except those presently believed to give the most accurate results. Consequently refinements of procedure were employed that can be mentioned here only in the most cursory fashion. It was stipulated that each method would be utilized in the manner believed by its practitioners to be the most dependable. In this there was just one limitation. Although it is our custom when using the thermometric method to determine both freezing and melting curves and to base judgments on the data obtained each way, it was decided in this instance to utilize for the official computations only those data obtained during freezing.

II. PREPARATION OF SAMPLES

1. Selection of materials

Benzene was chosen as the major constituent with knowledge that it had a number of disadvantages. Thus, in the fully dried state, it is an extreme desiccant. There is a long record of difficulties in determining its true melting point or triple point. On the other hand, its triple point is conveniently close to the triple point of water. Further, it was believed that some of the anomalies of its properties might be resolved during the investigation.

The choice of *n*-heptane as the contaminant was largely based upon the extreme difficulty of separating it from benzene by regular distillation. Although the boiling points of *n*-heptane and benzene are 18° apart, the boiling points of benzene and the azeotrope, which contains 0.7% of *n*-heptane, differ by only 0.1°C. All samples for the investigation were prepared to lie between benzene and the azeotrope. For this reason the fractionation of the samples even in an efficient still would be practically impossible. It can be totally neglected in connection with the transfers employed in this study. *n*-Heptane was chosen also because of a belief that its solution in liquid benzene would be ideal within the range of the measurements while it would be insoluble in frozen benzene.

2. Preparation of a "pure" benzene

As starting material, 2 liters of "ACS Reagent Grade" benzene, claimed by its producers to be "thiophene-free" and found to be of good quality, was chosen. This was further purified by 5 treatments with concentrated sulfuric acid lasting about 20 hours, and leachings with 5 portions of distilled water.

The benzene was transferred to a 2-liter distillation flask fitted by standard unlubricated glass joints to a Widmer column, condenser, adapter, and receiving flask. After about 250 ml of benzene and water had been slowly distilled, and without interruption of the boiling, the condenser, adapter, and receiver were replaced by a similar assembly of a dry condenser, adapter, and the ampoule D illustrated in Fig. 1. After 800 ml were distilled into the ampoule, the ampoule was disconnected from the condenser and stoppered.

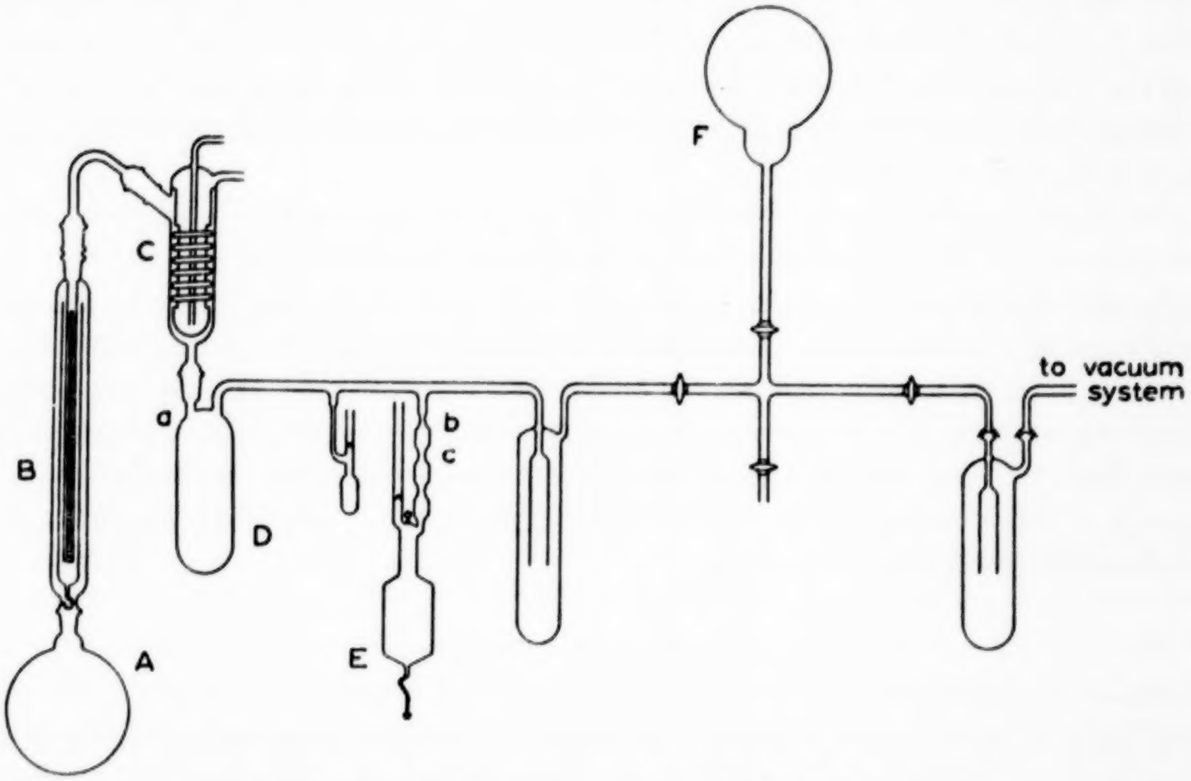

Fig. 1. Apparatus for filling the crystallization ampoule.

As the first stage of removing gases and water, the benzene in the ampoule D was frozen with a bath of solid carbon dioxide. During freezing, the pressure in the system was kept reduced by intermittent pumping. When the benzene was completely frozen, the system was sealed at *a* in Fig. 1. The benzene was then melted and refrozen slowly. The gases, including water, which were evolved during freezing, were pumped off from time to time by opening the ampoule to the ballast bulb F. When the ballast bulb was not open to the freezing benzene, the pressure in it was maintained at approximately 10^{-6} mm Hg by means of a mercury diffusion pump. After the benzene was completely solidified, it was subjected to the direct pumping of the diffusion pump for about half an hour during which time the glass of the system, wherever feasible, was heated with a soft flame. The benzene was melted and was refrozen while pumping in the same fashion as before. The benzene was again melted. The desired amount of benzene was transferred to ampoule E, by chilling the ampoule. This benzene was slowly frozen and degassed as before, chilled with liquid nitrogen and subjected to the direct action of the pump while the glass was again heated with a flame. The ampoule with its break-bulb was then sealed. Resinous ethylene glycol phthalate, which is considered as insoluble in benzene, was used on the stopcocks. Two samples of about 500 ml each were prepared as outlined.

Greatest reliance for the purification of the benzene was placed upon the growth of single crystals by a method developed by HORTON[3] and derived from that of TAMMANN or of BRIDGMAN. In HORTON's apparatus, Fig. 2, the large glass tube contains two immiscible liquids. Since convection occurs within each liquid but not across the interface, we were able to maintain a difference in temperature of approximately 60° across the interface of the two liquids, although the temperature distribution within each liquid was nearly uniform. The upper liquid was kept at about 30°C

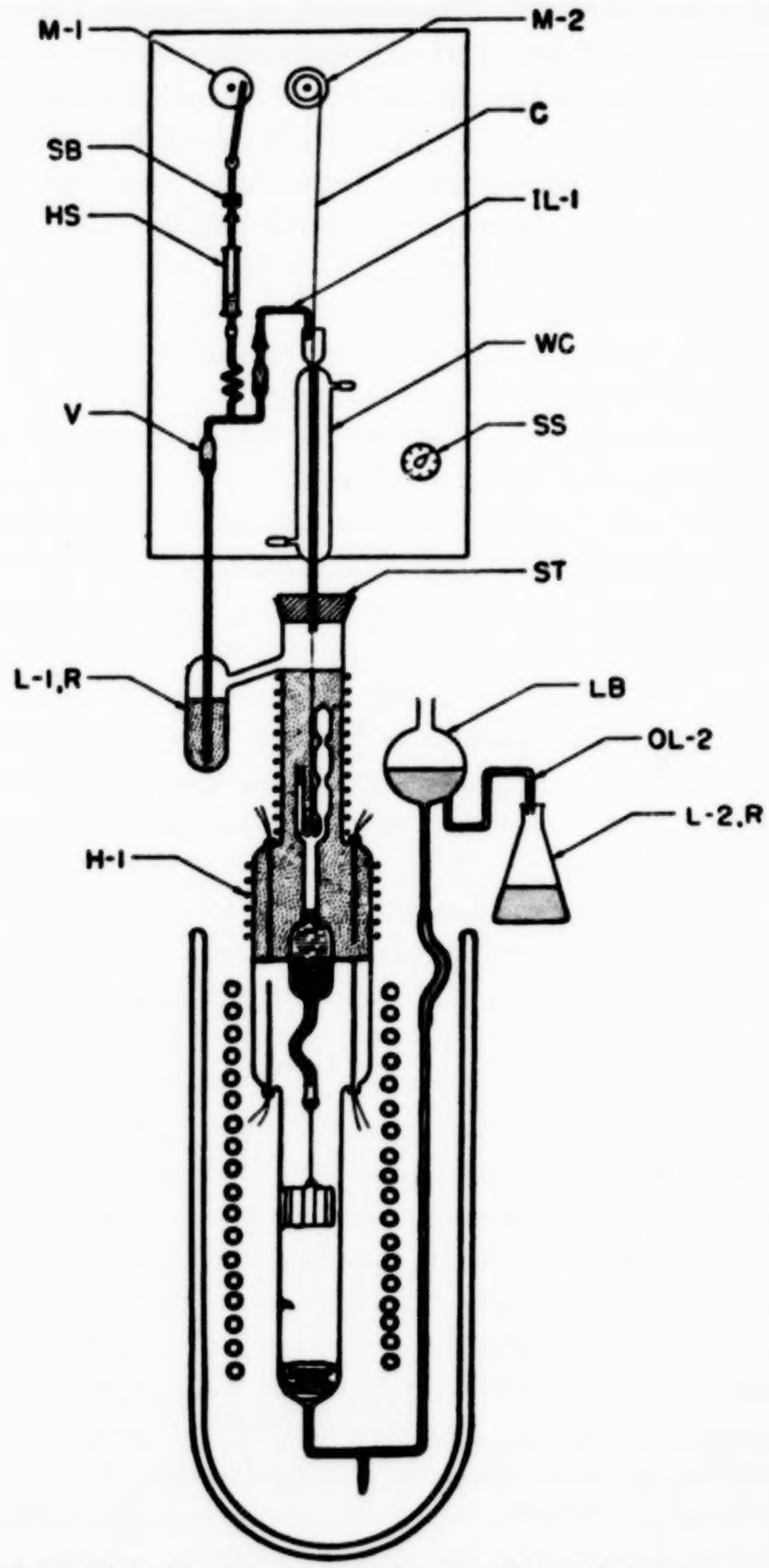

Fig. 2. Apparatus for growing single crystals of benzene.

by a coil of heating wire wound around the tube, and the lower liquid cooled to about —28°C by immersion in a refrigerated bath contained in a Dewar-type flask. During a period of about 10 days, the ampoule of benzene was lowered across the interface between the upper and lower liquids, the slow movement being controlled by a clock mechanism. Fig. 3 is a diagram of the apparatus. At the end of the 10 days, all but about 15 ml of the benzene had frozen. The ampoule was removed from the bath and clamped in an inverted position. Upon warming the surface of the vessel with the hands, the surface of the crystal and all of the solid in the crooked capillary melted and drained into one of the seal-off bulbs *b* of Fig. 1. Here it was chilled to the temperature of liquid nitrogen and sealed off from the rest of the sample. A second crystal was grown in the other ampoule. We believe the impurity in the two crystals of these samples to be less than can be disclosed by thermal analysis.

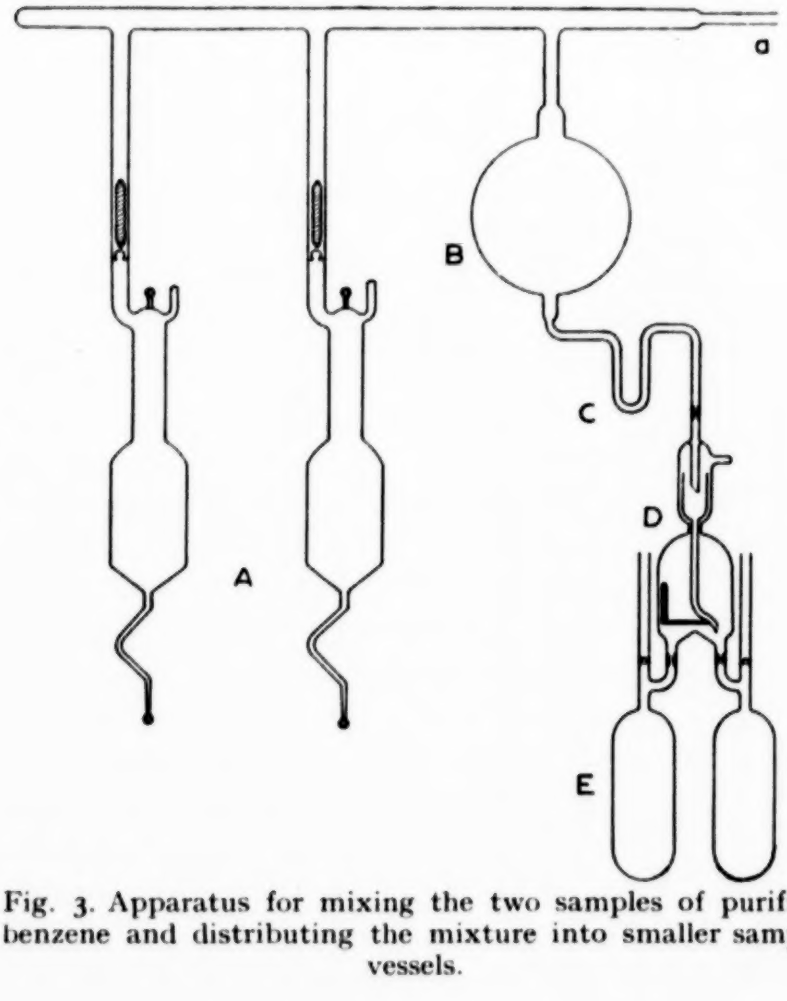

Fig. 3. Apparatus for mixing the two samples of purified benzene and distributing the mixture into smaller sample vessels.

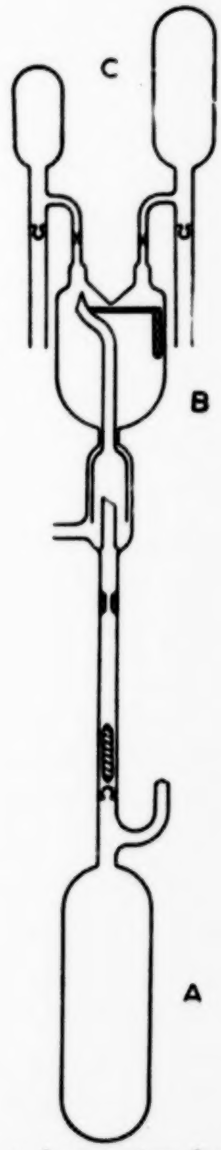

Fig. 4. Apparatus for the partitioning of samples for analysis (also used for introducing contaminant).

The material in these two ampoules was combined and divided into 4 parts. To do this, the ampoules were sealed into the system shown in Fig. 4. Over a period of several hours the system was evacuated with a diffusion pump while, from time to time, the glass was heated with a flame. The system was then closed by sealing off at *a*.

Liquid nitrogen was placed at trap C and solid carbon dioxide packed around the bulb B. The samples from separate single-crystal growing operations were combined in the bulb by opening the ampoules at the break-bulbs with a magnetic hammer. The major part of benzene distilled into the bulb, that which condensed in the trap serving as a form of stopcock. Finally, the benzene in the bulb was allowed to melt, the liquid nitrogen bath was removed from around trap C, and the benzene was allowed to flow through the magnetically controlled distributor D into ampoules. The ampoules were chilled with liquid nitrogen and sealed off. Four ampoules containing approximately 250 ml each were prepared.

3. Partition and contamination of the portions

The 4 ampoules prepared as described were divided, either with or without intentional contamination. The final samples were subsequently subjected to the thermometric and calorimetric methods of analysis. The contaminations and partitions were performed in the following manners. In one instance a group of thin-wall glass tubes about 10 cm long and somewhat less than 1 mm in bore was washed by putting them upright in a column in which dry, reagent-grade benzene was refluxed for about an hour. The tubes were then dried in a heated vacuum system. The internal diameters at both ends of the tubes were measured with a microscope and filar-micrometer eyepiece. Tubes selected for uniformity in diameter were weighed on a micro balance. NBS Standard Sample No. 216a *n*-heptane was introduced into 3 of these tubes by means of a micro-buret. The ends containing the *n*-heptane were then cooled with compact solid carbon dioxide; the tubes were exhausted and sealed off with a flame. The portion of the tube containing the *n*-heptane and the portion removed in sealing were weighed. The length of the liquid in each tube was measured with a travelling microscope, the sealed end of the tube and the meniscus of the liquid having nearly the same conformation. Thus two measurements were made of the amount of *n*-heptane in each tube. For a more highly contaminated sample, *n*-heptane was introduced in 3 of the fragile sample bulbs that are used in combustion calorimetry. The determination of the amount of contaminant was based solely on the comparative weights.

Apparatus shown in Fig. 5, is similar to that used to partition the original purified benzene, and was used to divide and contaminate the samples. The tube or bulb selected by the young woman not otherwise participating in the work was placed above the break-bulb of the ampoule. The system was pumped and flamed for about 2 hours before sealing. The tube or bulb of *n*-heptane and the break-bulb were broken by the same magnetic hammer. After steps were taken to assure thorough incorporation of the *n*-heptane into the benzene, the apparatus was inverted and each sample partitioned into ampoules containing 40, 80, and 100 ml by means of the magnetically controlled distributor. These ampoules were then sealed and removed in the usual fashion. One of the samples was divided without contamination. For simplicity of identification the uncontaminated sample was given the designation A, the first contaminated sample the designation B, and the second contaminated sample the designation C.

III. THERMOMETRIC ANALYSIS

1. Apparatus

The apparatus used in the determination of the purity of benzene from time-temperature freezing and melting curves is similar to the one developed by GLASGOW AND

TENENBAUM[4]. The cell and the completely assembled apparatus are shown in Figs. 6 and 7. The seeding devise was not used because preliminary experiments had shown that, in general, the small degree of undercooling exhibited by benzene made it unnecessary.

In order to minimize errors in the experiments, all components used in temperature measurement were carefully calibrated. The Meyers bifilar, helical, platinum resistance thermometer and the 10-ohm standard resistance used in the calibration of the Mueller G-2 bridge were calibrated at the National Bureau of Standards. During the course of the experiments, the thermometer was periodically checked against the triple point of pure water.

The triple-point cell was of the type used for calibrating thermometers, and the depth of immersion of the thermometer in the cell was 13 inches. A comparison of the triple point of water in this cell was made with that observed in the cell shown in Fig. 5 with 40 ml of water and with a depth of immersion of the thermometer of 2.8 inches. The results of this comparison are given in Table VIII.

Resistance readings were taken every minute. In addition to these manual readings the temperature was recorded in two fashions. The first consisted of amplifying the off-balance signal from the bridge by passing it through a DC high-gain amplifier (Liston-Becker Model No. 14). This amplified signal was fed into a Brown 10 millivolt recording potentiometer. In order to obtain both a manual and a printed continuous record of the same experiment, the signal from a copper-constantan thermocouple junction was balanced out by a Rubicon potentiometer to within 0.01 millivolt of the total signal generated at the freezing point. The residual signal was fed through the DC amplifier and into the recorder. The sensing junction of the couple was placed in the middle of the length of the platinum coil, between the glass case of the thermometer and the thermometer well. A triple-point water cell was used as the reference point. This cell was equipped with radiation shielding and insulated at the top with glass wool to stabilize it as much as possible. The entire potentiometer was thermally insulated so as to minimize thermal e.m.f.'s. Under these conditions it was possible to record to a precision of approximately 0.0001°C. This precision has been checked by using a triple point cell of diphenyl ether and one of water. The apparent overall drift over a period of 1 hour was found to be less than 0.00005°C.

The data, as given in this paper, were handled both by the methods given by TAYLOR AND ROSSINI[5] and by SCHWAB AND WICHERS[6]. Other procedures were employed by SAYLOR. Portions of these results will be reported in another paper.

2. *Experimental details*

Extreme care was exercised during the filling of the cell. The cell was cleaned with chromic acid, and carefully washed with distilled water. It was then evacuated with a mercury diffusion pump and subsequently heated to 150°C for a period of 24 hours. All samples were introduced by breaking the break-off tip of the containing ampoule and pouring the contents directly into the tube. In order to prevent any accidental contamination of the cell between runs, additional break-off tips were included in the manifold so that other samples could be introduced into the cell and investigated without letting air into the cell between runs. The samples were run in the following order: (1) two samples of A, (2) one of sample B, and (3) one of sample C.

The original size of sample was 50 ml. However, for a sample of this size, the freezing

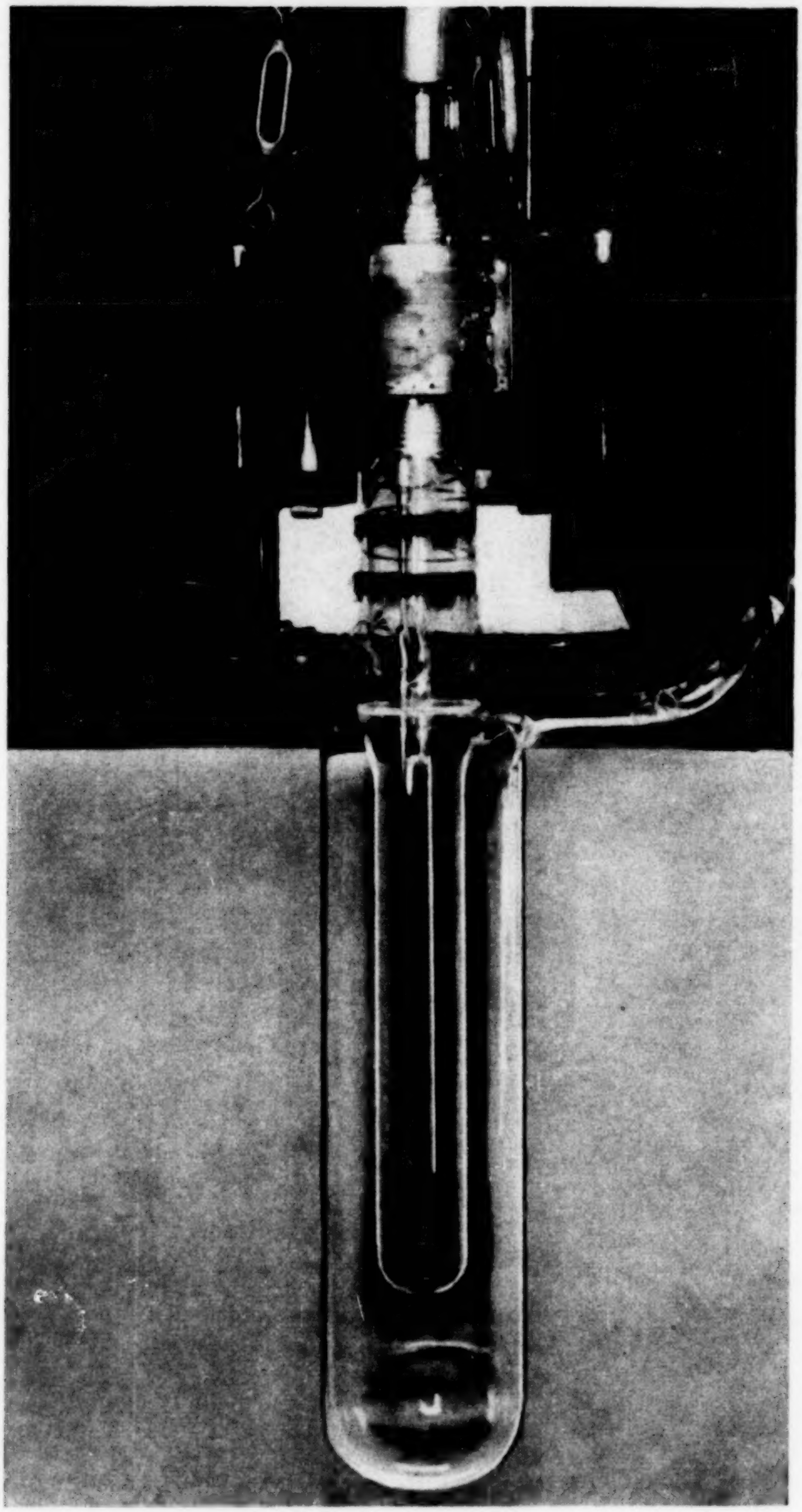

Fig. 5. Modified thermometric cell (silvering of the glass surface of the double-walled jacket, confining the evacuated space, was removed to show stirrer, thermometer well, and sample holder).

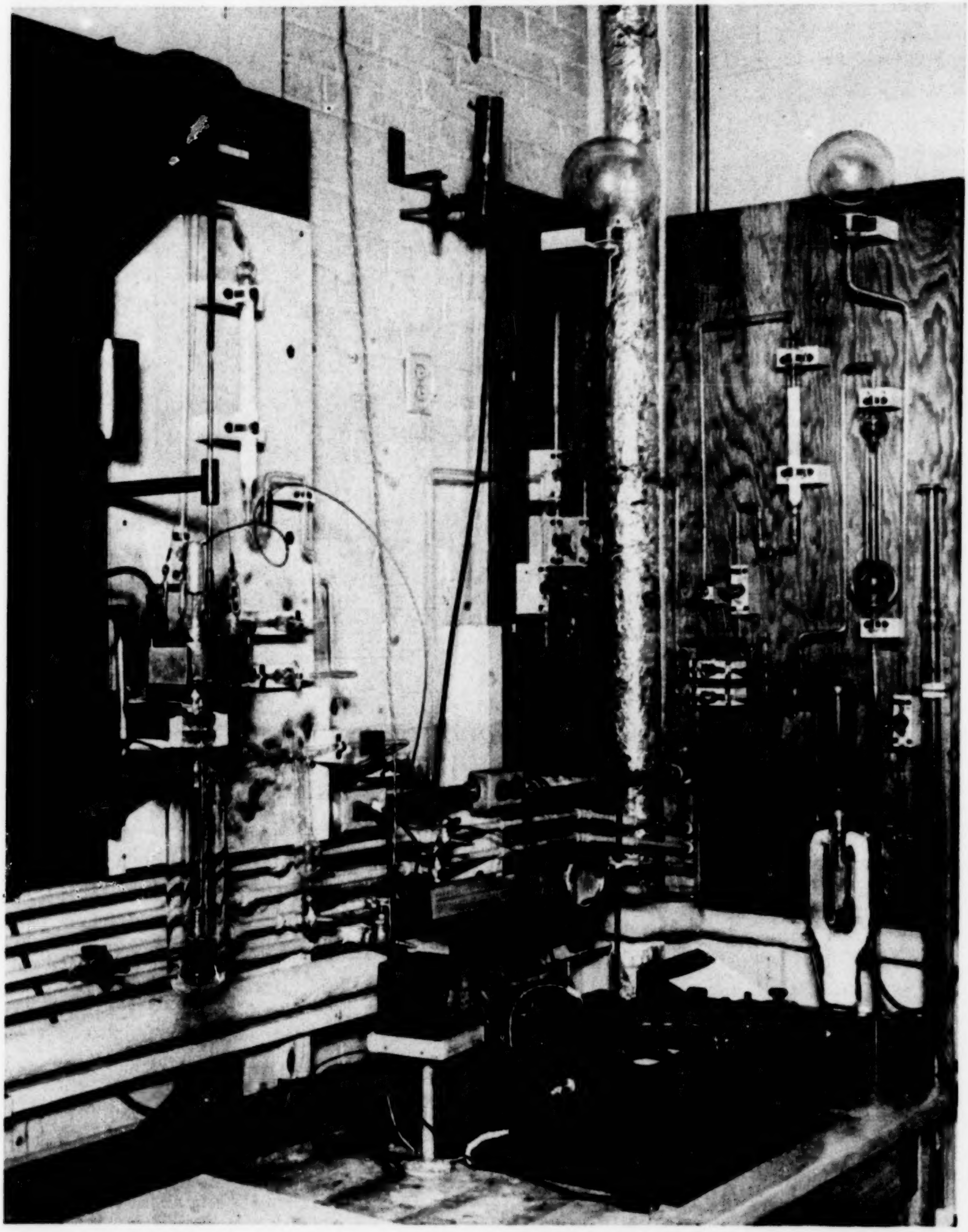

Fig. 6. Complete apparatus used in the measurement of purity by the thermometric method.

TABLE I

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE A-1[1]

Expt.	T_f^{tp}	$T_{f_0}^{tp}$	ΔT	N_2^*
1	278.6106	278.6188	0.0082	0.00012
2	278.6072	278.6090	0.0018	0.000027
3	278.6107	278.6366	0.0259	0.00039
5	278.6138	278.6391	0.0253	0.00039
6	278.6104	278.6325	0.0221	0.00034
7	278.6108	278.6400	0.0292	0.00044
8	278.6126	278.6367	0.0241	0.00037

$\overline{T}_f^{tp} = 278.6109 \pm 0.0020°\text{K}$	$\overline{T}_{f_0}^{tp} = 278.6304 \pm 0.0113°\text{K}$
Variance $= 423 \cdot 10^{-8}$	Variance $= 13918 \cdot 10^{-8}$
Standard deviation $= \pm 0.0021$	Standard deviation $= \pm 0.0118$

Purity[a] $= 99.97_0 \pm 0.02$ mole %
Purity[b] $= 99.90_5 \pm 0.006$ mole %
[1]Melting experiments on 50-ml sample.

experiments exhibited peculiarities which made analysis impossible. The sample would recover rapidly from undercooling, but then the observed temperature would rise steadily, although slowly, until the sample could no longer be stirred. For this reason, Table I shows only melting experiments. When the "melting" bath was placed around the cell the temperature was observed to fall very rapidly before commencing to rise. This erratic freezing behavior was suspected to be related to the size of the benzene sample, so auxiliary experiments were conducted in another similar cell with reagent grade benzene. The behavior was identical to the more pure benzene. Successive experiments were run wherein 10 ml fractions of the sample were removed. When the sample size approached 40 ml, a normal freezing behavior was noted.

TABLE II

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE A-2[1]

Expt.	T_f^{tp}	$T_{f_0}^{tp}$	ΔT	N_2^*
1	278.6690	278.6708	0.0018	0.000027
2	278.6686	278.6721	0.0035	0.000053
3	278.6682	278.6696	0.0014	0.000021
4	278.6670	278.6683	0.0013	0.000020
7	278.6683	278.6706	0.0023	0.000035
8	278.6693	278.6744	0.0051	0.000078
9	278.6680	278.6708	0.0028	0.000043
10	278.6679	278.6702	0.0023	0.000035

$\overline{T}_f^{tp} = 278.6683 \pm 0.0006°\text{K}$	$\overline{T}_{f_0}^{tp} = 278.6709 \pm 0.0014°\text{K}$
Variance $= 54 \cdot 10^{-8}$	Variance $= 254 \cdot 10^{-8}$
Standard deviation $= \pm 0.0007$	Standard deviation $= \pm 0.0016$

Purity[a] $= 99.99_6 \pm 0.002$ mole %
Purity[b] $= 99.99_3 \pm 0.002$ mole %
[1]Melting experiments on 50-ml sample.

The freezing curves, as obtained with this type of apparatus, are generally considered to be more reliable than the melting curves, and all subsequent measurements on the benzene consisted of freezing curves only, using a sample size of 40 ml. However, a comparison of Table II with Table III shows that there is no appreciable difference between the data obtained from melting experiments employing 50 ml of sample and freezing experiments employing only 40 ml of benzene.

As shown in Table I, the purity of the supposedly "pure" benzene is not appreciable high. We suspected that in some unexplained fashion we had contaminated the sample. We therefore removed this sample and introduced another identical sample into our cell, without allowing air to enter the cell at any time. Tables II and III show the results. Further investigation showed that the first sample was probably contaminated by water from the cell walls. This water could be considered as "chemi-adsorbed" in contrast to the "physi-adsorbed" water removed by the heating and pumping technique. In view of the relatively large surface area of the cell and the manifold, the observed lowering in temperature is not unduly large if attributed to water. From this experience, one might suspect that the benzene in the form of the large single crystal was much purer than the sample measured and could have been contaminated during the partition process. The partitioning of the samples were done after careful evacuation and "flaming" of all glass parts at approximately 350-400°C.

TABLE III

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE A-2[1]

Expt.	T_f^{tp}	$T_{f_0}^{tp}$	ΔT	N_2^*
1	278.6684	278.6745	0.0061	0.000093
2	278.6684	278.6718	0.0034	0.000052
3	278.6699	278.6732	0.0033	0.000050
4	278.6692	278.6744	0.0052	0.000079
5	278.6689	278.6734	0.0045	0.000068
6	278.6696	278.6714	0.0018	0.000027
7	278.6692	278.6718	0.0026	0.000040
8	278.6709	278.6736	0.0027	0.000041
9	278.6691	278.6716	0.0025	0.000038
10	278.6697	278.6729	0.0032	0.000049

$\overline{T}_f^{tp} = 278.6693 \pm 0.0005$°K
Variance $= 56 \cdot 10^{-8}$
Standard deviation $= \pm 0.0007$

$\overline{T}_{f_0}^{tp} = 278.6729 \pm 0.0008$°K
Variance $= 133 \cdot 10^{-8}$
Standard deviation $= \pm 0.0012$

Purity^{a,b} $= 99.99_4 \pm 0.002$ mole %

[1] Freezing experiments on 40-ml sample.

This higher temperature could account for the smaller contamination. When sample A-1 was transferred from the ampoule to the cell, the cell and manifold were dried by heating to 150°C while evacuating the system with a mercury diffusion pump backed by an oil mechanical fore-pump. However, the inclusion of several break-off tip seals in the permanent part of the manifold assemble attached to the cell made possible the introduction and removal of all subsequent samples without allowing the cell and permanent manifold to be open to the air. In this fashion, owing to the order in which the samples were run, the cell was in each case "conditioned" or purged by material of a higher purity than the sample being tested.

The portion of the manifold between the particular break-off tip being used and the new sample being introduced was thoroughly cleaned and dried by first heating and pumping, followed by a purging of this section with dry benzene. After the removal of this benzene, the break-off tips of the ampoule and the cell manifold were broken and the sample was poured into the cell. This technique of purging the entire system with benzene before introducing the next sample is thought to be necessary in order to assure non-contamination of the sample in the cell itself. All handlings of the samples were preceded by the distillation of a dry sample of benzene, using the manifold as a reflux column and condenser.

The data given in Table IV are those obtained from the analysis of the recorded thermocouple e.m.f. The curves indicate that much of the "randomness" exhibited by the

TABLE IV

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE C[1]

Expt.	T_f^{fp}	$T_{f_0}^{fp}$	ΔT	N_2^*
2	278.6288	278.6798	0.0510	0.000777
5	278.6325	278.6784	0.0459	0.000699
6	278.6386	278.6874	0.0488	0.000743
7	278.6342	278.6549	0.0207	0.000315
8	278.6342	278.6630	0.0288	0.000439
9	278.6346	278.6719	0.0373	0.000568
11	278.6364	278.6692	0.0328	0.000499
12	278.6366	278.6643	0.0277	0.000422
14	278.6360	278.6634	0.0274	0.000417
15	278.6358	278.6545	0.0187	0.000285

$\overline{T_f^{fp}} = 278.6348 \pm 0.0019\,^\circ$K
Variance = $719 \cdot 10^{-8}$
Standard deviation = ± 0.0027

$\overline{T_{f_0}^{fp}} = 278.6687 \pm 0.0024\,^\circ$K
Variance = $1166 \cdot 10^{-8}$
Standard deviation = ± 0.0034

Purity[a] = $99.94_8 \pm 0.004$ mole %
Purity[b] = $99.94_2 \pm 0.002$ mole %

[1] These freezing experiments on a 40-ml sample were machine recorded with a thermocouple as the sensing element. They were also manually recorded with a platinum thermometer as the sensing element. The manually recorded results on the same experiments are shown in Table VII.

TABLE V

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE B[1]

Expt.	T_f^{fp}	$T_{f_0}^{fp}$	ΔT	N_2^*
1	278.6512	278.6575	0.0063	0.000096
2	278.6505	278.6566	0.0061	0.000093

$\overline{T_f^{fp}} = 278.6509\,^\circ$K
$\overline{T_{f_0}^{fp}} = 278.6570\,^\circ$K

Purity[a] = 99.99_1 mole %
Purity[b] = 99.96_8 mole %

[1] These freezing experiments on 40 ml of benzene were machine recorded with a platinum resistance thermometer as the sensing element.

manual recording of points is not random. Since the thermocouple is small and lies next to the thermometer well, it is more sensitive to local changes, and the departures as shown by the recorded trace are larger in magnitude than those manually recorded. The divergence of the two curves, as increasing amounts of sample are frozen, is considered to arise from the difference between local effects sensed by the thermocouple and the larger overall effect sensed by the thermometer. Since the thermocouple was not accurately calibrated, the data in Table IV give only a relative comparison. Table V, which shows the results of recording the resistance of the platinum thermometer itself does not have this restraint, and may be directly compared with values as given in the manually recorded experiments. The fluctuations observed on the machine-recorded data can readily be shown to be real changes. The true fitting of these recorded curves should give better accuracy and precision, since a fit of the manually recorded values is limited by the necessary assumption that the scatter is random.

3. Correlation and explanation of data

In order to reduce individual errors a rather large number of experiments have been run on each sample. In these, the freezing bath was always a solid carbon dioxide slush. The bath immersion was kept constant throughout all experiments. The rate of cooling of the liquid benzene was varied between 0.3° and 0.5° per minute. The warming bath used in the melting experiments was water maintained at 25°C. These melting experiments took place over a longer period of time and the liquid warming rate was varied between 0.1° and 0.3° per minute.

All curves which were capable of mathematical analysis are given. Some freezing curves exhibited the peculiarity of having a constant slope, and since these are not capable of mathematical interpretation they are not included. Five experiments on sample A and four on sample B exhibited this tendency.

TABLE VI

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE B[1]

Expt.	T_f^{tp}	$T_{f_0}^{tp}$	ΔT	N_2^*
1	278.6564	278.6594	0.0030	0.000046
2	278.6488	278.6562	0.0074	0.000113
3	278.6526	278.6819	0.0293	0.000446
4	278.6559	278.6697	0.0138	0.000210
5	278.6534	278.6794	0.0260	0.000396
6	278.6527	278.6810	0.0283	0.000432
7	278.6518	278.6733	0.0215	0.000327
8	278.6553	278.6936	0.0383	0.000583
9	278.6550	278.6732	0.0182	0.000277
10	278.6524	278.6607	0.0083	0.000126
11	278.6514	278.6901	0.0387	0.000589
12	278.6488	278.6640	0.0152	0.000231

$\overline{T_f^{tp}}$ = 278.6529 ±0.0016°K
Variance = $628 \cdot 10^{-8}$
Standard deviation = ±0.0025

$\overline{T_{f_0}^{tp}}$ = 278.6735 ±0.0077°K
Variance = $14528 \cdot 10^{-8}$
Standard deviation = ±0.0120

Purity[a] = 99.96_9 ±0.014 mole %
Purity[b] = 99.97_0 ±0.004 mole %

[1] Freezing experiments on 40-ml sample.

In Tables I-VII, purity is calculated using two different $T_{f_0}{}^{tp}$'s. When the purity is listed as "purity^a", this signifies that the $T_{f_0}{}^{tp}$ used is that obtained by averaging the calculated $T_{f_0}{}^{tp}$'s for the group of experiments listed in the table above the value. The "best" or most probable value of $T_{f_0}{}^{tp}$ is considered to be the average of the experiments listed in Table III, and purity, as calculated using this value, is listed as "purity^b". The value of the cryoscopic constant A, $\dfrac{\Delta H_f}{RT_{f_0}{}^2}$, which was used in this calculation is the A.S.T.M. value of 0.01523 degrees^{-1}. The minor difference in the value as reported in the following section of this paper is not enough to change the purity values listed herein.

The calculation of the mole fraction of the total amount of impurity present in each sample, $N_2{}^*$, was made by using the following equation:

$$N_2{}^* = A(T_{f_0}{}^{tp} - T_f{}^{tp}) \qquad (1)$$

This simplified equation was derived on the assumption that it is valid only when the total mole fraction of impurity is small and only when all the impurity remains in the liquid phase during crystallization and forms an ideal solution with the major component.

TABLE VII

RESULTS OF THERMOMETRIC ANALYSIS OF BENZENE, SAMPLE C[1]

Expt.	$T_f{}^{tp}$	$T_{f_0}{}^{tp}$	ΔT	$N_2{}^*$
1	278.6311	278.6551	0.0240	0.00036
2	278.6327	278.7313	0.0986	0.00150
3	278.6341	278.6727	0.0386	0.00059
4	278.6339	278.6655	0.0316	0.00048
5	278.6341	278.6650	0.0309	0.00047
6	278.6331	278.6548	0.0217	0.00033
7	278.6356	278.6606	0.0250	0.00038
8	278.6336	278.6595	0.0259	0.00039
9	278.6339	278.6645	0.0306	0.00047
10	278.6351	278.6674	0.0323	0.00049
11	278.6364	278.6771	0.0407	0.00062
12	278.6337	278.6628	0.0291	0.00044
13	278.6331	278.7041	0.0710	0.00108
14	278.6329	278.6478	0.0149	0.00023
15	278.6344	278.6631	0.0287	0.00044
16	278.6332	278.6566	0.0234	0.00036

$\overline{T}_f{}^{tp} = 278.6338 \pm 0.0007\,^\circ\mathrm{K}$
Variance $= 153 \cdot 10^{-8}$
Standard deviation $= \pm 0.0012$

$\overline{T}_{f_0}{}^{tp} = 278.6692 \pm 0.0112\,^\circ\mathrm{K}$
Variance $= 43415 \cdot 10^{-8}$
Standard deviation $= \pm 0.0208$

Purity^a $= 99.94_6 \pm 0.018$ mole %
Purity^b $= 99.94_0 \pm 0.002$ mole %

[1] Freezing experiments on 40-ml sample.

The data is tabulated showing the purity and delta temperature as calculated for each experiment as well as a purity value determined by the average $T_{f_0}{}^{tp}$ and the $T_{f_0}{}^{tp}$ obtained on the second sample of A which is considered to be the best value. The calculation of the variance and standard deviation is straightforward. The uncertainty is given in terms of each sample and indicates the probable percision (95% confidence level) as calculated by usual statistical methods. All temperatures are given in terms of degrees Kelvin and were obtained by adding the constant 273.16 to the $T_f{}^{tp}$ and $T_{f_0}{}^{tp}$ values originally calculated in terms of degrees Celsius.

There is no readily apparent explanation for $T_{f_0}{}^{tp}$ as calculated from these experiments being lower than previously reported values.

TABLE VIII

CALIBRATIONS AND RELIANCE LIMITS OF RESULTS GIVEN IN TABLES I-VII

H_2O (triple-point measurements)

(A) In normal triple point cell (13-inch immersion)
  (1) at time of sample A-1
  $R = 25.4818_{37} \pm 0.000010$ abs. ohms
  (2) at time of sample A-2
  $R = 25.4818_{04} \pm 0.000010$ abs. ohms
  (3) at time of sample B
  $R = 25.4818_{62} \pm 0.000010$ abs. ohms
  (4) at time of sample C
  $R = 25.4818_{42} \pm 0.000010$ abs. ohms

(B) 40 ml distilled and degassed H_2O in freezing point apparatus (2 experiments performed after running sample C)
  (1) $R = 25.4818_{00} \pm 0.000018$ abs. ohms
  (2) $R = 25.4818_{11} \pm 0.000016$ abs. ohms

Bridge and thermometer calibrations

(A) For ice triple point — $(N\text{-}R)/2$ varies between limits of 0.002207 and 0.002246 abs. ohms with average of 0.0022_{19}.
(B) For benzene samples — $(N\text{-}R)/2$ varies between limits of 0.02221 and 0.02269 with average of 0.02245.
(C) The change in the bridge calibration between start and finish of these experiments is not known, but, in view of previous calibrations, the change is probably less than —0.000030 abs. ohms. Such a change is of the same order as the precision in a single calibration.

Reliability of reported T_{f_0}'s and T_f's of benzene samples

(A) Assuming an accumulative propagation of error, the absolute value of the $T_{f_0}{}^{tp}$ of benzene should be $5.51_{29} \pm 0.002$°C.
(B) In terms of the above, the absolute values of the $T_f{}^{tp}$'s reported would also have the same limits of accuracy.
(C) The errors as expressed above are of the order of magnitude necessary to account for the standard deviations obtained in those experiments relating to sample A-2.

IV. CALORIMETRIC ANALYSIS

1. Method

The calorimetric method for determining the chemical purity of benzene involved the measurements of liquid-solid equilibrium temperatures at various precisely known liquid to solid ratios evaluated from the total heat input, heat of fusion, and heat capacity. The measurements of liquid-solid equilibrium temperatures were made under conditions of saturation vapor pressure of benzene. The method requires considerably more equipment than the thermometric method but offers an advantage in that the equilibrium temperature can be measured at one's leisure. If temperature equilibrium is not indicated, then a longer time can be allowed, within reason, until a temperature equilibrium is attained. Recently, the calorimeters of this laboratory have been provided with automatic adiabatic controls which conveniently permit long equilibrium times. Previously, when the calorimeters were controlled manually to attain the adiabatic condition, the maximum conveniently allowable equilibrium time was about 2 hours. In the experiments described in this paper, at least 16 hours have been allowed per measurement in order to attain more closely the liquid-solid equilibrium conditions.

For a substance of high purity, the relation for thermodynamic equilibrium between the pure crystal and the liquid containing mole fraction impurity N_2 may be given by the simplified equation:

$$N_2 = A(T_{f_0}^{tp} - T_{obs}) \quad \ldots\ldots \quad (2)$$

where

A = $\Delta H_{f_0}/R[T_{f_0}^{tp}]^2$, the cryoscopic constant,
ΔH_{f_0} = the heat of fusion at $T_{f_0}^{tp}$,
R = the gas constant,
$T_{f_0}^{tp}$ = the triple-point temperature of the pure substance, and
T_{obs} = the observed liquid-solid equilibrium temperature.

When this high-purity substance containing total mole fraction N_2^* of liquid-soluble, solid-insoluble impurity is partially crystallized, the concentration of the impurity in the liquid phase is greater by the ratio $1/F$, where F is the fraction melted. The mole fraction impurity of the solution in equilibrium with the crystal is then given by:

$$N_2 = N_2^*(1/F) \quad \ldots\ldots \quad (3)$$

and when equations (2) and (3) are combined,

$$(N_2/A) = (N_2^*/A)(1/F) = T_{f_0}^{tp} - T_{obs} \quad \ldots\ldots \quad (4)$$

Equation (4) shows that the plot of T_{obs} with respect to $1/F$ is a straight line and that, when $1/F = 0$, $N_2 = 0$ and the temperature intercept is the triple-point temperature of the pure material. The slope (N_2^*/A) of the line determines the total mole fraction impurity of the material.

2. *Apparatus*

Determinations of the purity of benzene were made in an adiabatic calorimeter designed for heat-capacity measurements in the range 10° to 300°K on substances that can be readily transferred by vaporization[7]. Fig. 7 shows a schematic drawing of the calorimeter.

The sample container, suspended in the calorimeter by a thin-walled monel filling tube, was constructed chiefly of copper with a capacity of about 106 ml. In order to provide as uniform a distribution of energy as possible to the enclosed sample, tinned copper vanes were arranged radially from the central re-entrant well, containing a heater and an encapsulated platinum-resistance thermometer, to the outer wall of the

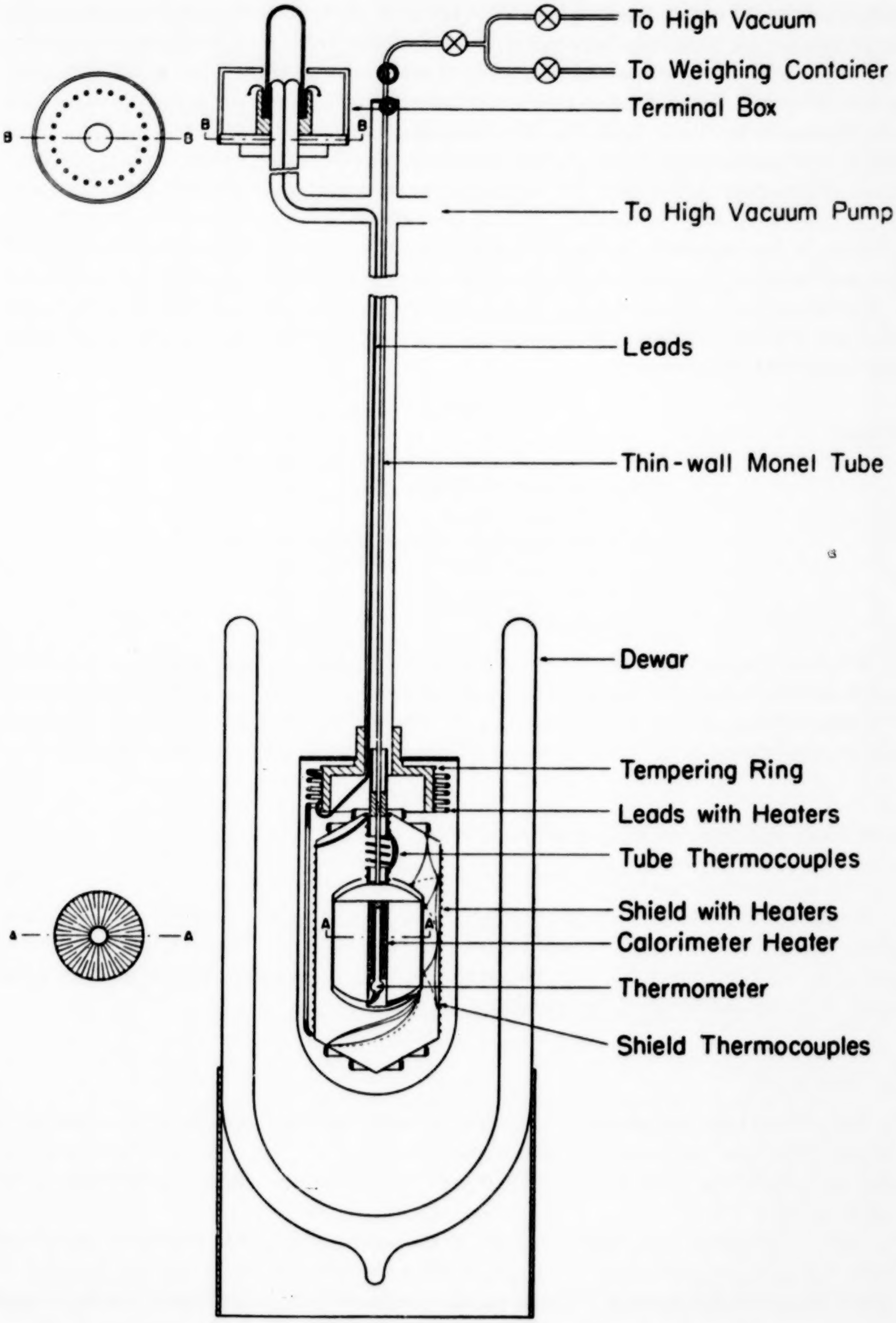
To High Vacuum
To Weighing Container
Terminal Box
B
B
B
B
To High Vacuum Pump
Leads
Thin-wall Monel Tube
Dewar
Tempering Ring
Leads with Heaters
Tube Thermocouples
Shield with Heaters
Calorimeter Heater
Thermometer
Shield Thermocouples
A
A
A
A

Fig. 7. Adiabatic calorimeter for volatile substances.

container. The vanes were held in place by means of a thin coating of pure tin applied to the interior surfaces of the container and so spaced that the maximum separation was about 4 millimeters. The tin afforded an inert surface to benzene.

A thin copper thermal shell attached to the upper periphery of the container afforded a nearly isothermal surface, regardless of any localized temperature differences on the surface of the container, to the adiabatic shield surrounding the container and the shell. Electronic control equipment was used to adjust the currents in the several shield heaters so that the temperature of the shield could be automatically maintained at the same temperature as that of the shell. Sensitive thermocouples placed between the shield and the shell controlled the operation of the electronic system. The outer surface of the container, the inner and outer surfaces of the shell, and the inner surface of the adiabatic shield were gold-plated and polished to minimize heat transfer by radiation. A high vacuum (10^{-6} mm Hg) was maintained in the space surrounding the sample container and the adiabatic shield.

The resistance of the platinum thermometer, having the ice-point resistance of about 25.5 ohms, was measured by means of a special Mueller bridge designed for the range of 0.00000 to 422.11110 ohms. The platinum-resistance thermometer was calibrated in accordance with the 1948 International Temperature Scale[8]. The temperatures in degrees Kelvin were obtained by adding 273.1600 degrees to the temperatures in degrees Celsius*.

The electrical input energy was determined from the measurements of the current and potential across the 100 ohm Constantan wire heater and the time interval of heating. The heater current and potential were determined by means of a Wenner potentiometer in conjunction with a standard resistor and a volt box. The time-interval of heating was measured by means of a precision interval timer operated on a standard frequency of 60 cycles furnished by the Time Laboratory of the Bureau. The timer has been compared periodically with standard second signals and found to vary not more than ±0.02 second per heating period, which was never less than 6 minutes. All electrical instruments have been calibrated in terms of the standards maintained at the National Bureau of Standards.

3. *Experimental procedure*

Oil-diffusion vacuum pumps were used in conjunction with suitable mechanical vacuum pumps to evacuate the calorimeter and the various accessory equipment. The vacuum manifolds contained liquid nitrogen traps to prevent back diffusion of oil into the apparatus being evacuated. The general procedure for evacuating an apparatus was to maintain it for at least 24 hours at 100°C and at 10^{-6} mm Hg as registered at the vacuum manifold. Although the resistance to gaseous flow was minimized, some of the equipment necessarily contained valves and small diameter tubulations, particularly the weighing flasks and the calorimeter container.

---

* The temperatures given are believed to be accurate to ±0.01 degree Kelvin. Wherever temperatures are given to four decimal figures, the last two digits are significant only in the measurement of small temperature differences.

At the Tenth General Conference held in 1954, the General Conference on Weights and Measures adopted a new definition of the thermodynamic temperature scale by assigning the temperature 273.16°K to the triple-point temperature of water. For details regarding the adoption of this new scale, see reference[9].

Each sample of benzene was vacuum-distilled directly from the ampoule, in which it was received, into a separate weighing container fitted with a valve. After weighing, the container was attached to the calorimeter transfer manifold and the entire sample vacuum-distilled into the sample container. When the purity of the uncontaminated sample (sample A), which was investigated first, was found to be 99.99_{37} mole %, a purity considerably lower than anticipated, the weighing containers and all transfer manifolds were thoroughly purged with portions of the sample A and then pumped to a high vacuum before transferring the subsequent samples. The evacuation of the system for 24 hours at 100°C and at 10^{-6} mm Hg at the vacuum manifold was considered to be still insufficient when working with extremely pure substances. Repeated purging and evacuation were thought to be helpful in cleaning the system. Since another sample of the purest material was not available, tests could not be made to determine whether the sample A had been contaminated during the transfer to the calorimeter.

The experimental procedure for making the purity measurements was the following. The heat capacity of the system containing the sample was determined in the range from about 250° to 290°K. Then, the heat of fusion was determined by introducing a known quantity of electrical energy sufficient to raise the temperature of the system from just below to just above the triple point and making corrections for the heat capacity and for the premelting due to the presence of impurity.

The liquid-solid equilibrium temperatures were determined as follows. To avoid local concentration of the impurities, which was considered possible by slow cooling methods, the sample was rapidly crystallized either in part or in whole, taking the precaution to maintain the filling tube temperature considerably above the melting point of the sample so that the sample would not condense in the tube. When the sample was partially crystallized, it was allowed to equilibrate by bringing the adiabatic shield into automatic control. When the sample was totally crystallized, it was heated electrically under adiabatic control to the desired liquid-solid ratio and allowed to equilibrate. It was convenient to allow the sample to equilibrate over-night and to observe the liquid-solid equilibrium temperatures during the morning of the following day. After the liquid-solid equilibrium temperature was established, a known quantity of electrical energy was added sufficient to raise the temperature of the sample to just above the triple point. If Q is the electrical energy that was added, then $Q - \int C\mathrm{d}T$ is the energy required to melt the material from the observed equilibrium temperature. The term $\int C\mathrm{d}T$ is the heat-capacity correction. Then,

$$1/F = \frac{L_f}{L_f - (Q - \int C\mathrm{d}T)} \quad \ldots\ldots\ldots\ldots \quad (5)$$

where L_f is the total heat of fusion. In this method any small heat leak that may occur during the prolonged equilibrium interval would not affect the $1/F$ value.

4. *Results*

The results of the measurements of heat of fusion on the benzene samples are given in Table IX. The results compare favorably with the selected value (9837 abs j mole^{-1}) given by ROSSINI *et al.*[10]. Since sample B was somewhat larger than generally used in the calorimeter, it was felt that a small amount of the sample could have been condensed in the tube during the heat-of-fusion measurements. When measurements on all the

TABLE IX

HEAT OF FUSION OF THE BENZENE SAMPLES

Molecular weight = 78.1140 g; °K = °C + 273.16°

Temperature interval of heating °*K*	*Total energy input* *abs j*	*Corrections* *heat capacity* *abs j*	*premelting* *abs j*	L_f *Total* *abs j*	ΔH_f *abs j mole*$^{-1}$
Sample A, mass of sample = 76.6591 g					
274.9985 to 282.2772	11005.6	1357.1	10.6	9659.1	9842.4
275.8612 to 281.2168	10650.4	998.4	13.9	9665.9	9849.3
275.7011 to 280.8662	10611.4	961.2	13.1	9663.3	9846.7
275.6013 to 282.2809	10899.3	1247.8	12.7	9664.2	9847.5
271.1321 to 281.4924	11556.2	1907.9	5.1	9653.4	9836.6
		Mean			9844.5
		Standard deviation of the mean[a]			±2.3
Sample B, mass of sample = 90.3655 g					
260.7869 to 281.5943	15601.4	4214.2	4.5	11391.7	9847.2
Sample B, mass of sample = 76.0445 g					
261.1786 to 282.3869	13401.5	3824.8	3.9	9580.6	9841.3
		Mean			9844.2
		Standard deviation of the mean			±3.0
Sample C, mass of sample = 86.3014 g					
268.5729 to 281.0443	13345.9	2499.7	35.6	10881.8	9849.4
257.9009 to 280.7212	15296.1	4452.5	16.7	10860.3	9830.0
271.6529 to 281.3753	12785.3	1957.0	52.0	10880.3	9848.1
		Mean			9842.5
		Standard deviation of the mean			±6.3

[a] Standard deviation of the mean as used above is defined as $[\Sigma d^2/n(n-1)]^{1/2}$: where d is the difference between a single observation and the mean, and *n* is the number of observations.

TABLE X

LIQUID-SOLID EQUILIBRIUM TEMPERATURES OF BENZENE, SAMPLE A

$1/F$	*Treatment of sample*[a]	T_{obs}[b] °*K*	T_{calc} °*K*	$T_{obs} - T_{calc}$ °*K*
8.844	*H*	278.6450	278.6445	0.0005
7.703	*C*	278.6486	278.6492	−0.0006
5.051	*C*	278.6603	278.6601	0.0002
3.165	*C*	278.6672	278.6679	−0.0007
2.221	*H*	278.6718	278.6718	0.0000
2.088	*C*	278.6720	278.6723	−0.0003
1.287	*C*	278.6762	278.6756	0.0006
1.000			278.6768	

Triple-point temperature, 278.6809°K or 5.5209°C.
Slope, −0.00411F°K.
Impurity, 0.0063 ±0.0010 mole %[c].

[a] The symbol *C* indicates that the sample was rapidly crystallized and the symbol *H* indicates that the sample was rapidly crystallized and heated to the $1/F$ values given.

[b] These temperatures were obtained from the relation °K = °C + 273.1600° and are believed to be accurate to ±0.01°K. The last two decimal places are significant only in the measurement of small temperature differences.

[c] The uncertainty was estimated by examining the imprecision of the measurements and all known sources of systematic error. The system was assumed to follow the ideal solution law and to form no solid solution with the impurity.

samples were completed, the heat-of-fusion measurements were repeated using about 84 % of the original sample B. The results indicate that a negligible amount, if any, was in the tube during the first measurements.

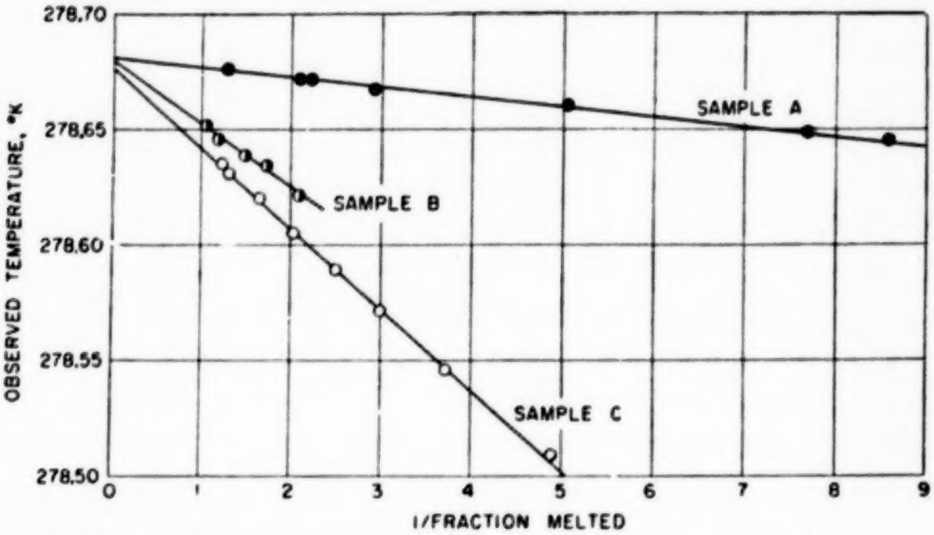

Fig. 8. Liquid-solid equilibrium temperatures of the benzene samples at various $1/F$ values

The observed liquid-solid equilibrium temperatures and the corresponding $1/F$ values are summarized in Tables X, XI, and XII, for the benzene samples A, B and C, respectively, and are plotted together in Fig. 8. The values of temperatures given in column 4 of these tables were calculated from equation (4) using the values of N_2^* and $T_{f_0}^{tp}$ as determined from a linear equation fitted to the experimental data by the method of least squares. The comparison of calculated and observed liquid-solid equilibrium temperatures gives an indication of thermodynamic equilibrium, of ideality of the solution, and of formation of solid solution in the range of the experiments.

The cryoscopic constant used in the various calculations was 0.01525(°K)$^{-1}$, based on the triple-point temperature, $T_{f_0}^{tp}$, and the mean heat of fusion obtained on the

TABLE XI

LIQUID-SOLID EQUILIBRIUM TEMPERATURES OF BENZENE, SAMPLE B

$1/F$	*Treatment of sample*[a]	T_{obs}[b] °K	T_{calc} °K	$T_{obs} - T_{calc}$
2.100	*H*	278.6212	278.6221	—0.0009
1.735	*H*	278.6339	278.6322	0.0017
1.484	*H*	278.6387	278.6391	—0.0004
1.187	*H*	278.6458	278.6473	—0.0015
1.047	*H*	278.6518	278.6511	0.0007
1.000			278.6525	

Triple-point temperature, 278.6799°K or 5.5199°C.
Slope, —0.0275F°K.
Impurity, 0.042 ±0.005 mole %[c].

[a] See footnote a, Table X.
[b] See footnote b, Table X.
[c] See footnote c, Table X.

purest sample A. The values obtained with sample A are considered to be the most nearly accurate. The $T_{f_0}{}^{tp}$ value 278.6809°K, when reconverted to degrees Celsius, becomes 5.5209°C. Considering the imprecision of the measurements and the various sources of errors, the uncertainty in the value of 5.5209°C for the triple-point temperature of pure benzene was estimated to be ±0.0050°C including the uncertainty of ± 0.0030°C in the determination of the temperature. MATHIEU[11] reported the value 5.524°C for the triple-point temperature of pure benzene.

The samples were allowed to equilibrate at least 16 hours, and the temperatures observed during the next 4 hours did not change in any instance by more than 0.0002 degree. The prior treatment of the sample, whether it was partially crystallized rapidly or totally crystallized rapidly and melted to the desired $1/F$ value, did not seem to give any definite trend in the results. The deviations of the observed liquid-solid equilibrium temperatures from the calculated values are scattered and are somewhat larger than those observed in previous investigations in which successive liquid-solid temperatures were observed during a single day by melting the same crystal stepwise and allowing shorter time intervals (about 1 to 2 hours) for equilibrium [12,13]. The measurements of the temperature using the same bridge and thermometer over a relatively short range of temperature, are considered to be reproducible within about 0.0002° from day to day. The observed deviations greater than these amounts may arise from the differences in the crystallization process[14], although the crystallization was thought to be well controlled, and the non-equilibrium conditions even after 16 hours. Since the calorimeter was operated at a temperature very close to room temperature, a small amount of benzene and *n*-heptane may have condensed in the filling tube during the long equilibrium period. Both benzene and *n*-heptane have sufficient vapor pressure at 5°C to condense on the tube if any portion of the tube is colder than the sample container. The contribution to the deviation from this source, however, is considered

TABLE XII

LIQUID-SOLID EQUILIBRIUM TEMPERATURE OF BENZENE, SAMPLE C

$1/F$	*Treatment of sample*[a]	T_{obs}[b] °K	T_{calc} °K	$T_{obs} - T_{calc}$ °K
4.905	*C*	278.5092	278.5072	0.0020
3.733	*H*	278.5461	278.5476	—0.0015
2.998	*C*	278.5716	278.5729	—0.0013
2.492	*H*	278.5891	278.5903	—0.0012
2.040	*H*	278.6054	278.6059	—0.0005
1.651	*H*	278.6201	278.6193	0.0008
1.321	*C*	278.6312	278.6307	0.0005
1.226	*C*	278.6350	278.6340	0.0010
1.000			278.6418	

Triple-point temperature, 278.6764°K or 5.5164°C.
Slope, —0.0346F°K.
Impurity, 0.053 ±0.005 mole %[c].

[a] See footnote a, Table X.
[b] See footnote b, Table X.
[c] See footnote c, Table X.

to be fairly small, unless there is a preferential condensation of *n*-heptane, which is unlikely.

A series of controlled experiments is required to resolve these small differences. Continuous measurements of the liquid-solid equilibrium temperatures could be made at various $1/F$ values by successively melting a crystal formed by both rapid crystallization and by slow crystallization. These measurements could be made at equilibrium times equivalent to those involved in manually controlled measurements and at the prolonged equilibrium times possible in automatic controlled measurements. At the writing of this report sufficient data have not been accumulated on these measurements for presentation.

V. CONCLUSIONS

The analyses by thermometric and calorimetric procedures can now be compared with the anticipated purities based upon the methods of preparing the three samples A, B, and C. For this, the assumptions are made that the uncontaminated benzene was pure beyond any power of either method to disclose the impurity and that the contaminations had proceeded exactly in accord with the plans and calculations.

Table XIII shows two effects that were unexpected before the final assemblage of data. These effects can serve as valuable guides to future work, however. First, the large divergence between the thermometric and the calorimetric analyses that had characterized earlier comparisons, both in our own laboratories and elsewhere, is not displayed. The differences between the analyses on all three samples are roughly of the order of the statistically estimated uncertainties of the averages and less than deviations between individual experiments by one method. The inherent evidences of accuracy are good and both groups of workers completed their tasks with a sense of confidence. Second, both forms of analysis gave results that differed significantly from values computed by the amount of contaminant that had been added.

TABLE XIII

COMPARISON OF THE RESULTS FROM THERMOMETRIC AND CALORIMETRIC ANALYSES WITH THE VALUES COMPUTED FROM CONTAMINATION

Sample	*Purity, mole %*			*Excess of purity computed from amount of deliberate contamination above average of analysis by thermometric and calorimetric processes*
	Computed from contamination	*Thermometric analysis*	*Calorimetric analysis*	
A	100[a]	99.99_4 ±0.002	99.9937 ±0.0010[b]	0.006
B	99.9964	99.97_0 ±0.004	99.958 ±0.005[b]	0.032
C	99.9610	99.94_0 ±0.002	99.947 ±0.005[b]	0.017

[a] The "pure" sample was assumed to be pure beyond the sensitivity of the methods of analysis employed.

[b] See footnote c, Table X.

It should not be too surprising that the earlier differences between the methods should have become much reduced. Both sets of analyses were performed under the conditions mentioned in the introduction — "that each method would be utilized in the manner believed by its practitioners to be most dependable." The result is that there were significant modifications of procedure or interpretation of data by both groups.

In the thermometric experiments the greatest change, except for refinements of temperature measurement were modifications of the means of interpreting data. It has been known that, when $T_{f_0}{}^{tp}$ is calculated by the method of TAYLOR AND ROSSINI, the values become progressively higher as purer samples are employed. In the present work, although the same fundamental method is used, slightly modified criteria were employed to select the usable portion of a freezing curve and for calculation both of ideal and actual points of initial freezing.

In the calorimetric analyses the principle changes were experimental, there being two important changes of technique. The time of equilibration was greatly increased both to attain temperature stability and to allow diffusion of impurities within the liquid phase. Furthermore, the thermal history of each run was changed in such ways that very little separation of the impurities from the rest of the sample could occur.

On the second point, the difference between the analyses and the assumed purity of the samples as prepared and contaminated, an important clue is found in data of Table I. The first two runs were made on a Friday after the benzene had been introduced into the freshly heated and exhausted apparatus. The sealed apparatus remained unused until the following week when the other runs were made and a much larger amount of impurity was disclosed. On this basis subsequent runs were made by conditioning the interior of the apparatus with benzene of high purity. This can account for the difference between Table I and those that follow. Observing, both on the assumed "pure" sample and on the several contaminated samples, that the impurities found exceeded those anticipated more or less in relation to the number of times that a benzene sample had been introduced into a flamed and exhausted glass vessel without contact with air, it is beguiling to infer that flaming with exhaustion does not adequately prepare glass to receive benzene without contaminating it.

In the body of the paper it was suggested that chemi-sorbed water might be a source of contamination. This inference was drawn before the assemblage of data disclosed the difference between assumed and determined purities. Whether it is true or not may possibly be disclosed by experiments now in progress, but in any event the evidence is strong that it is difficult to manipulate benzene in glass in such manner as to preserve a state of high purity. The results of this investigation strongly indicate that additional series of closely controlled experiments need be performed to determine (a) the source of discrepancies previously found between the thermometric and calorimetric methods of analysis and (b) the sources of contamination during the handling of the benzene samples.

SUMMARY

Workers at the National Bureau of Standards and elsewhere have been conscious of the discordant results sometimes yielded by two methods for determining purity employing the same physical principle. A comparison was made on samples of benzene by the thermometeric method, by which a stirred sample is frozen at nearly constant rate, and by the calorimetric method, by which a frozen sample is melted in stages by the addition of accurately controlled increments of energy under adiabatic conditions.

Benzene, purified by single crystal formation and of very high purity, was contaminated in known amounts by *n*-heptane and samples of the same level of purity determined by both procedures. Great care was taken to submit samples of the same composition to the different groups employing the two different methods. Further, the actual degree of contamination of the benzene was unknown to both groups until final values of the purity were submitted.

Results of this comparison showed that the large divergence between the two methods that had characterized earlier comparisons is not displayed. The differences between the analyses on all three samples are roughly of the order of the statistically estimated uncertainties of the averages and less than deviations between individual experiments by one method.

Comparison of the methods with absolute values of purity could not be made because of contamination of the highly purified sample of benzene with supposedly chemically adsorbed water from the borosilicate glass walls.

RÉSUMÉ

Des chercheurs au Bureau National des Étalons des États Unis et ailleurs se sont rendu compte du fait que l'on obtient parfois des résultats discordants lorsque l'on détermine une pureté par deux méthodes basées sur le même principe physique. Dans ce mémoire on décrit une comparaison de déterminations de puretés d'échantillons de benzène d'une part par la méthode thermométrique au cours de laquelle un échantillon agité est congelé à une vitesse à peu près constante et, d'autre part, par la méthode calorimétrique où l'on fait fondre un échantillon congelé en étappes en lui fournissant des portions d'énergie exactement réglées sous des conditions adiabatiques.

Du benzène purifié par formation de cristaux et d'une très haute pureté a été contaminé par des quantités connues de *n*-heptane et des échantillons d'un même degré de pureté ont été examinés par les deux procédés. L'on a pris grand soin de soumettre des échantillons de même composition aux différentes équipes employant les deux méthodes différentes. De plus, les vrais degrés de contaminations du benzène étaient inconnus aux deux équipes jusqu'à ce que les valeurs définitives de puretés furent soumises.

Les résultats de cette comparaison ont montré que les grandes divergences entre les deux méthodes qui avaient caractérisé les comparaisons plus anciennes ne se produisaient pas. Les différences entre les résultats des analyses de tous les trois échantillons sont, approximativement, de l'ordre des incertitudes des valeurs moyennes estimées statistiquement; elles sont inférieures aux déviations entre les expériences individuelles par une seule méthode.

Une comparaison des méthodes donnant des valeurs de pureté absolues n'a pas pu être faite à cause de la contamination des échantillons hautement purifiés de benzène par de l'eau que l'on suppose être adsorbée chimiquement à partir du borosilicate des parois de verre.

ZUSAMMENFASSUNG

Forscher im ,,National Bureau of Standards'' und anderswo waren sich davon bewusst, dass man manchmal nicht übereinstimmende Resultate erhält wenn man den Reinheitsgrad mit zwei verschiedenen Methoden, die sich auf dasselbe physikalische Prinzip gründen, bestimmt. Ein Vergleich solcher Bestimmungen an Benzolproben wurde nun angestellt, und zwar einerseits mit Hilfe der thermometrischen Methode bei der eine gerührte Probe mit nahezu konstanter Geschwindigkeit zum Gefrieren gebracht wird, andererseits mit der kalorimetrischen Methode bei welcher eine gefrorene Probe in Etappen durch Zuführen genau geregelter Energiemengen unter adiabatischen Bedingungen geschmolzen wird.

Durch Einzelkristallbildung gereinigtes Benzol von hohem Reinheitsgrad wurde mit bekannten Mengen *n*-Heptan verunreinigt und Proben von gleichem Reinheitsgrade wurden nach beiden Verfahren geprüft. Es wurde besonders darauf geachtet, dass die verschiedenen Arbeitsgruppen, die die verschiedenen Verfahren anwendeten, Proben von gleicher Zusammensetzung erhielten. Ausserdem war der wirkliche Verunreinigungsgrad des Benzols beiden Gruppen solange unbekannt, bis die endgültigen Reinheitswerte mitgeteilt waren.

Die Ergebnisse dieses Vergleiches zeigten, dass die grossen Abweichungen zwischen den beiden Methoden, welche frühere Vergleiche kennzeichneten, nicht auftreten. Die Unterschiede zwischen den Analysen aller dreier Proben waren im grossen und ganzen von der Grössenordnung der statistisch geschätzten Unsicherheiten der Mittelwerte; sie waren kleiner als die Abweichungen zwischen den einzelnen mit einer selben Methode ausgeführten Versuchen.

Ein Vergleich der Methoden mit absoluten Reinheitswerten konnte nicht gemacht werden, weil das hoch gereinigte Benzol durch wahrscheinlich chemisch adsorbiertes Wasser aus dem Borosilikat der Glaswände verunreinigt wird.

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REFERENCES

[1] M. R. CINES, *Physical Chemistry of the Hydrocarbons*, Vol. I, Academic Press Inc., New York, 1950, p. 315.

[2] M.-P. MATHIEU, *Acad. roy. Belg., Classe sci., Mém.*, 28 (1953) Fasc. 2, No. 1639.

[3] A. T. HORTON, *U.S. Patent No.* 2, 754, 180, July 10, 1956.

[4] A. R. GLASGOW, JR. AND M. TENENBAUM, *Anal. Chem.*, 28 (1956) 1907.

[5] W. J. TAYLOR AND F. D. ROSSINI, *J. Research Natl. Bur. Standards*, 32 (1944) 197.

[6] F. W. SCHWAB AND E. WICHERS, *Temperature, its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, 1941, p. 256.

[7] R. B. SCOTT, R. D. RANDS, JR., C. H. MEYERS, F. G. BRICKWEDDE AND N. BEKKEDAHL, *J. Research Natl. Bur. Standards*, 35 (1945) 39.

[8] H. F. STIMSON, *J. Research Natl. Bur. Standards*, 42 (1949) 209.

[9] H. F. STIMSON, *Am. J. Phys.*, 23 (1955) 614.

[10] F. D. ROSSINI, K. S. PITZER, R. L. ARNETT, R. M. BRAUN AND G. C. PIMENTEL, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953.

[11] M.-P. MATHIEU, *Bull. soc. chim. Belges*, 61 (1952) 683.

[12] G. T. FURUKAWA, D. C. GINNINGS, R. E. MCCOSKEY AND R. A. NELSON, *J. Research Natl. Bur. Standards*, 46 (1951) 195.

[13] T. B. DOUGLAS, G. T. FURUKAWA, R. E. MCCOSKEY AND A. F. BALL, *J. Research Natl. Bur. Standards*, 53 (1954) 139.

[14] J. P. MCCULLOUGH, paper presented at the *Eleventh Calorimetry Conference, Johns Hopkins University, September 14 and 15, 1956*.

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MELTING-POINT PURITY DETERMINATIONS: LIMITATIONS AS EVIDENCED BY CALORIMETRIC STUDIES IN THE MELTING REGION*

by

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I. INTRODUCTION

Of present-day methods for determining the purity of organic substances, those that depend upon the effect of impurity on melting point are most reliable and best developed. There are three principal reasons for the wide-spread use of melting-point depression as a measure of purity. First, the melting-point depression is a colligative property, and chemical identification of the impurity is unnecessary. Second, analyses of experimental results can usually be made reliably by application of well-known theories of dilute solutions. Third, the required physical measurements — of temperature and of time or energy — can be made with high precision and reproducibility. For these reasons melting-point methods can be used to detect small concentrations of unknown impurity — as small as 0.001 mole % under favorable conditions — and are most useful in studies of very pure samples for which other methods often fail.

Comprehensive articles on modern techniques for determination of purity by melting-point studies have been published by ROSSINI and coworkers[1], CINES[2] and MATHIEU[3]. In 1947, the late HUGH M. HUFFMAN discussed the problem of purity determination, with particular emphasis on the calorimetric method used in this Laboratory[4]. HUFFMAN stressed the uncertainties inherent in any of the experimental methods then in use. He expressed doubt that the conditions realized in practice were always consistent with the basic assumptions made in analysing experimental results. Since the time of HUFFMAN's discussion, the accumulation of data in this Laboratory has confirmed many of his doubts and has led to a clearer understanding of the limitations of methods for melting-point purity determinations.

The two most important experimental methods are the dynamic (time-temperature) method[1,3] and the static (calorimetric) method[2,5]. Although each of these methods has unique advantages and disadvantages, both should give equivalent results under ideal conditions; the fact that they often do not is one of the reasons for reexaming the inherent limitations of melting-point purity techniques. The limitations of the calorimetric method, in particular, and their significance are the primary concern of this paper. Because limitations will be stressed, it should be

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emphasized at the outset that calorimetric studies usually are the most accurate means for detecting small amounts of impurity. The concern of this paper will be with the fact that, in some cases, impurity values may be in error by as much as a factor of 5. Such a large uncertainty in ***impurity*** generally corresponds to less than 0.1% uncertainty in *purity*.

To provide a basis for discussion, the experimental method used is in this Laboratory and some typical results will be given first.

II. EXPERIMENTAL

A. The apparatus

All measurements were made in precision adiabatic calorimetric systems described by HUFFMAN and co-workers[5]. In an experimental study about 55 ml of material is sealed under its own vapor pressure in either a copper or platinum calorimeter that contains horizontal, perforated metal disks spaced 2 mm apart to promote thermal equilibration and prevent settling of the solid phase during fusion experiments. The calorimeters are provided with a re-entrant well into which is soldered a platinum capsule containing a 55 Ω (at 0°C) platinum-resistance thermometer element and a 200 Ω constantan heater element[5c]. The resistance thermometers were calibrated on the International Temperature Scale of 1948[6] by comparison with standard thermometers calibrated at the National Bureau of Standards. Measurements of resistance and potential were made in terms of devices calibrated at the National Bureau of Standards.

B. The procedure

The low-temperature calorimetric equipment in this Laboratory is used primarily in the determination of entropy and other thermodynamic properties of pure substances. Measurements are made of heat capacity in the solid and liquid states between 11 and 380°K and of the latent heats and temperatures of the solid-solid and solid-liquid phase changes that occur in this temperature range. Also, the purity of each sample studied is determined from an investigation of the melting point. Only the procedure used for the melting-point studies will be described here.

1. *Crystallization.* — For studies of thermodynamic properties in the solid state it is necessary to ensure that samples are completely crystallized. In past work in this Laboratory, the same crystallization technique has been used before melting-point studies as before any other calorimetric measurements on the solid phase. Because experience has shown that it is difficult to crystallize many substances completely, a somewhat involved routine procedure has been adopted that is successful in most instances. The sample is cooled rapidly (1 to 2 deg. min^{-1}) until crystallization begins. After crystallization is essentially complete, the sample is allowed to cool to about 90°K in a 12 hour period. Next, it is heated to the melting point, and 5 to 10% is melted. The sample is held at the melting point for about 8 hours and then allowed to recrystallize and cool to about 30° below the melting point in a 12 hour period. In all, this routine procedure requires about 48 hours, during which time the sample is at or very near the melting point for about 12 hours.

2. *Observational procedure.* — After crystallization, a measured amount of energy, sufficient to melt 10% of the sample, is supplied to the calorimeter. The temperature

of the sample is then observed periodically until it becomes constant. In the same way, the temperatures corresponding to 25, 50, 70 and 90% of the sample in the liquid state are determined. The sample is then completely melted and heated 5 to 10° above the melting point. The results provide a melting curve. All observations are made under adiabatic conditions so that a value of the heat of fusion may be calculated from the results. (Generally, separate heat of fusion experiments are made before a melting-point study.) It has been found necessary to observe the temperature for *at least* one hour after each fraction of the sample is melted. Usually, the temperature is considered to be "constant" if the rate of change is 0.00003 deg. min^{-1} or less for 20 to 30 min. In some cases, the temperature decreases for the entire period of observation, while in others the temperature fluctuates in a 0.0002° range over a 20 to 30 min period.

A different technique has been employed occasionally to determine melting curves, with interesting results to be discussed later. The sample is *partly* crystallized (25 to 50% in the liquid state), and allowed to come to equilibrium. After the equilibrium temperature has been determined, successive fractions of the sample are melted and additional temperature observations are made as described previously. Determinations by this technique will be arbitrarily termed *freezing-point* studies to distinguish them from the customary *melting-point* studies that are preceded by careful and *complete* crystallization.

3. *Calculation of results.* — From the observations described in the preceeding paragraphs, values of the equilibrium melting temperature, T_{obsd}, are obtained as a function of the fraction of total sample melted, F. A plot is made of T_{obsd} *vs.* $1/F$, and the triple point temperature, $T_{\text{T.P.}}$, is determined by linear extrapolation to zero value of $1/F$ [7]. The mole fraction of total impurity, N_2^*, is calculated from the relationship

$$N_2^* = AF\,(T_{\text{T.P.}} - T_{\text{obsd}}) \qquad \text{(1)}$$

where A is the cryoscopic constant, $\Delta H_{\text{fusion}}/RT_{\text{T.P.}}^2$, and ΔH_{fusion} is the latent heat of fusion. This procedure is based on the four assumptions (1) that the values of T_{obsd} are thermodynamic equilibrium temperatures, (2) that an ideal solution is formed in the liquid phase, (3) that the impurity is insoluble in the solid phase and (4) that $N_2^* << 1$. Departure from linearity in a plot of T_{obsd} *vs.* $1/F$ may be taken as an indication that one or more of these basic conditions is not met fully.

C. Typical results

Since the establishment of this Laboratory in 1944, the calorimetric method has been used to determine the melting point and purity of over 125 samples of organic compounds ranging in purity from 99.6 to 99.999 mole %. The materials studied include hydrocarbons of various types and hydrocarbon derivatives containing nitrogen, oxygen, fluorine, sulfur and lead. From the results of these investigations, examples have been chosen to illustrate both the reliability of the calorimetric method and, in particular, its inherent limitations.

1. *Benzotrifluoride and 1-heptanethiol.* — Very few of the melting curves obtained are linear over the entire range of $1/F$ values as would be expected if equation (1)

were applicable. However, about 1/3 of the curves show only slight departure from linearity — chiefly at high values of $1/F$. The melting curve of benzotrifluoride[8] (Table I and Fig. 1) is linear within 0.0002°, which is not surprising since the sample contained only 0.001 mole % impurity. A more typical example of melting curves that are nearly, but not quite, linear is given by the results of four separate melting-point studies on a sample of 1-heptanethiol[8] (Table II and Fig. 2).

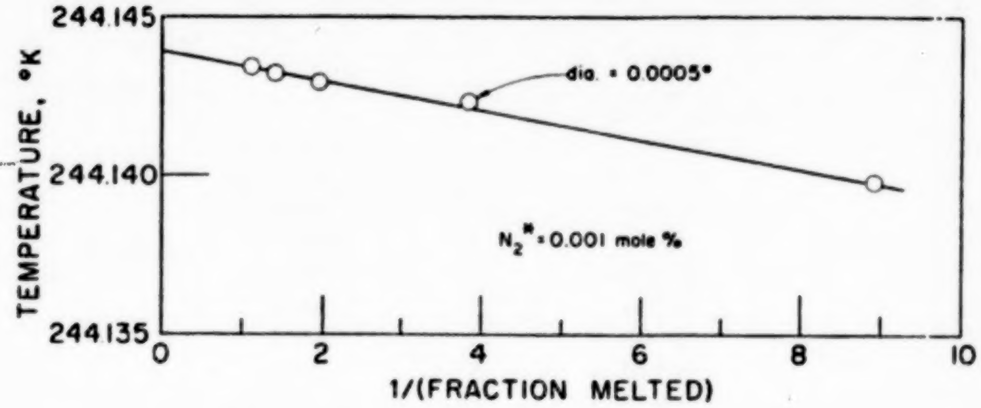

Fig. 1. The melting curve (T_{obs} vs. $1/F$) of benzotrifluoride.

TABLE I

BENZOTRIFLUORIDE: MELTING-POINT SUMMARY

$T_{T.P.} = 244.14 \pm 0.05$°K; $A = 0.02781$ deg.$^{-1}$;
$N_2^* = 0.001$ mole %[b]

Melted, %	*1/F*	*T, °K*	
		Obsd.	*calcd.*[b]
11.21	8.921	244.1398[a]	244.1398
26.14	3.826	.1423	.1421
50.98	1.962	.1429	.1430
70.86	1.411	.1432	.1433
90.75	1.102	.1434[a]	.1434
100.00	1.000		.1434
Pure	0		.1439

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain $T_{T.P.}$

[b] Calculated from the slope of the straight line of footnote *a* by use of equation (1).

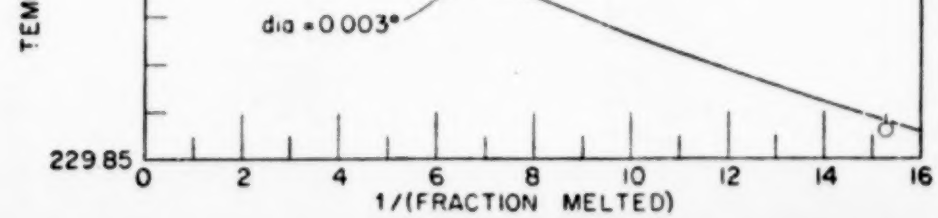

Fig. 2. The melting curve of 1-heptanethiol; the different symbols indicate results of four separate determinations.

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TABLE II

1-HEPTANETHIOL: MELTING POINT SUMMARY

$T_{\text{T.P.}} = 229.93 \pm 0.05°\text{K}$; $A = 0.05775$ deg.$^{-1}$;
$N_2^* = 0.04$ mole %[c]

Melted, %[a]	*1/F*	*T, °K*	
		Obsd.	*Graph.*[b]
2.648^1	37.76	229.7626	
6.544^1	15.28	.8559	229.8578
12.99^1	7.698	.8868	.8857
15.38^4	6.502	.8881	.8907
17.96^1	5.568	.8981	.8955
22.94^1	4.359	.9049	.9020
25.69^3	3.893	.9013	.9044
35.13^4	2.847	.9082	.9103
50.78^3	1.969	.9138	.9152
65.36^4	1.530	.9174	.9180
70.85^3	1.411	.9188	.9188
84.36^2	1.185	.9206	.9203
90.92^3	1.100	.9196	.9209
95.58^4	1.046	.9211	.9213
100.00	1.000		.9217
Pure	0		.9290

[a] Superscripts indicate points from four separate determinations.
[b] Temperatures read from a smooth curve through a plot of T_{obsd} *vs.* $1/F$.
[c] Calculated by use of equation (1) from the slope of the curve of footnote *b* between $1/F = 1.000$ and $1/F = 0$.

2. *Cycloheptatriene.* — The results for at least half the samples studied show moderate to pronounced deviation from linearity in plots of T_{obsd} *vs.* $1/F$—a possible indication of the formation of a solid-solution of the impurity in the major component. In some cases, the solid-solution treatment developed by FINKE[9] and by MASTRANGELO AND DORNTE[10] adequately accounts for observed non-linear melting curves. The results given for cycloheptatriene[11] in Table III and Fig. 3 illustrate the application of the solid-solution treatment.

TABLE III

CYCLOHEPTATRIENE: MELTING POINT SUMMARY

$T_{\text{T.P.}} = 197.92 \pm 0.05°\text{K}$[b]; $A = 0.003564$ deg.$^{-1}$;
$K = 0.128$[a]; $N_2^* = 0.0143$ mole %[b]

Melted, %	*1/F*	*T, °K*	
		Obsd.	*Calcd.*[b]
11.49	8.703	197.7655	197.764
25.36	3.943	.8167	.817
49.85	2.006	.8543	.855
70.49	1.419	.8692	.870
89.11	1.122	.8789	.878
100.00	1.000		.882
Pure	0		.917

[a] *K* is the Henry's Law constant for distribution of impurity between the solid and liquid phases.
[b] Calculated from the relationship[10] $T_F = T_{\text{T.P.}} - (N_2^*/A)/[F + K/(1 - K)]$.

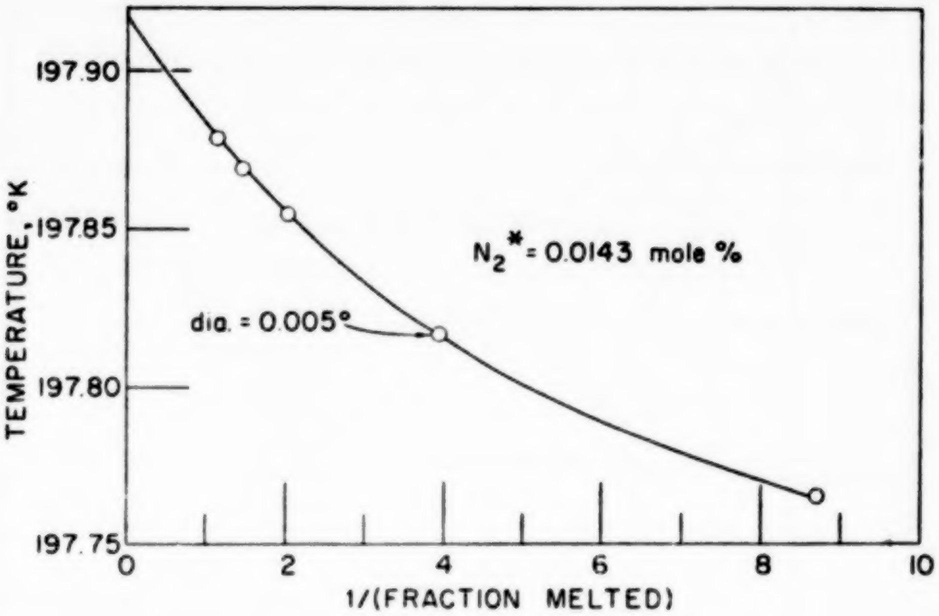

Fig. 3. The melting curve of cycloheptatriene.

3. *Pyrrole.* — The melting curves of some of the samples studied in this Laboratory have been determined both by the normal melting-point technique and by the modified "freezing-point" procedure (section II.B.2). In every case investigated to date, the "freezing" curve is significantly lower than the melting curve, as shown by the results for pyrrole[8] given in Table IV and Fig. 4.

The results of the melting-point study on pyrrole (curve B in Fig. 4) also illustrate an anomaly that has been observed in several other instances. The value of T_{obsd} at $1/F = 1.104$ is essentially the same as that at $1/F = 1.431$, and is significantly lower than an extrapolation of the melting curve based on results at the higher values of $1/F$.

TABLE IV

PYRROLE: MELTING POINT SUMMARY

Melted, %	*1/F*	*T, °K* *Obsd.*	*Calcd.*[b]
A. "Freezing" Point			
	$T_{\text{T.P.}} = 249.74_9 \pm 0.05$°K; $A = 0.01525$ deg.$^{-1}$; $N_2^* = 0.015$ mole %[b]		
40.36	2.478	249.7245[a]	249.7245
80.39	1.244	.7365[a]	.7365
100.00	1.000		.7388
Pure	0		.7485
B. Melting Point			
	$T_{\text{T.P.}} = 249.74_5 \pm 0.05$°K; $N_2^* = 0.006$ mole %[b]		
10.84	9.225	249.7075	249.7092
25.59	3.908	.7301[a]	.7301
49.21	2.032	.7377	.7374
69.89	1.431	.7398[a]	.7398
90.57	1.104	.7397	.7411
100.00	1.000		.7415
Pure	0		.7454

[a], [b] See footnotes Table I.

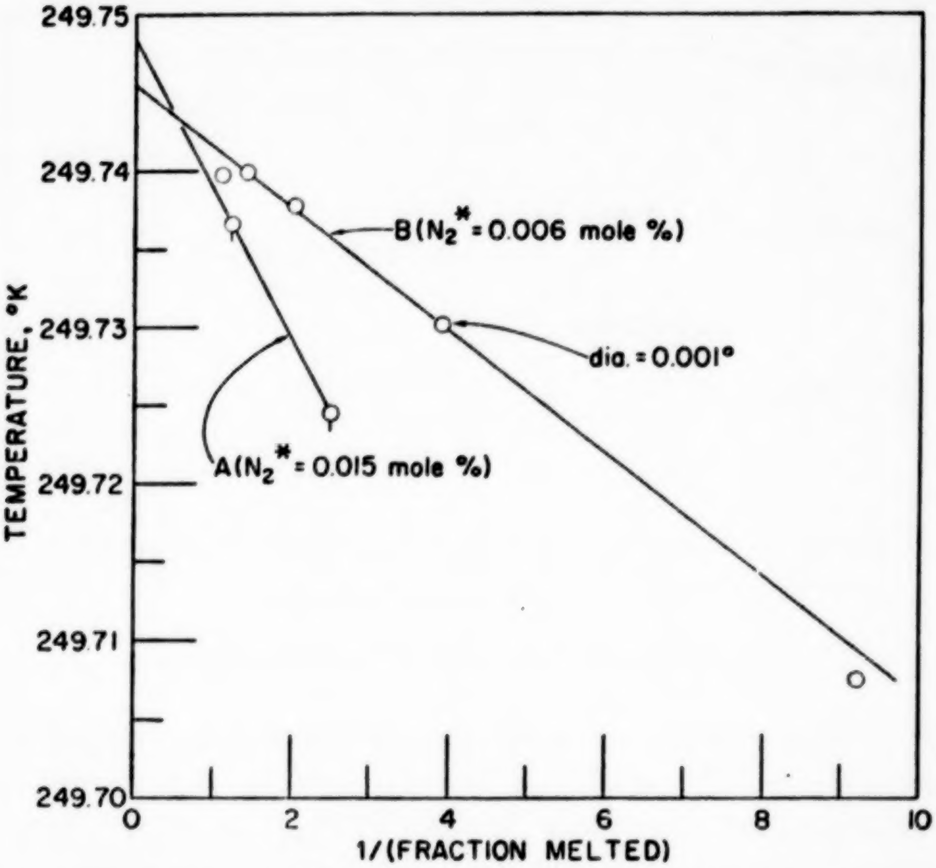

Fig. 4. The melting curves of pyrrole: A, results of a "freezing-point" study; B, results of a normal melting-point study.

4. *Cyclopentyl-1-thiaethane.* — Results of two melting-point studies on a sample of cyclopentyl-1-thiaethane[8] (methyl cylopentyl sulfide) are given in Table V and Fig. 5. At high values of 1/F the values of T_{obsd} determined in the two studies differ by about 0.01° although the precision of the results from either determination is about ± 0.0002°. Also, the values for the amount of impurity in the sample calculated from the results of the two studies differ by a factor of three.

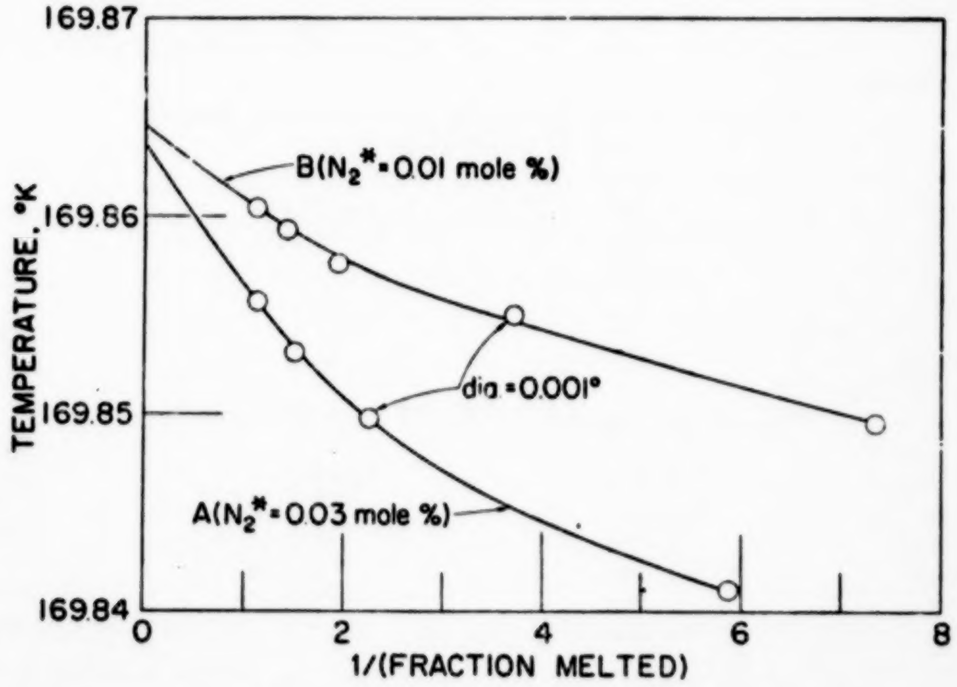

Fig. 5. The melting curves of cyclopentyl-1-thiaethane: A, results obtained after relatively "fast" crystallization; B, results obtained after slow crystallization.

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TABLE V

CYCLOPENTYL-1-THIAETHANE: MELTING POINT SUMMARY

Melted, %	*1/F*	*T, °K* *Obsd.*	*Calcd.*[b]
A. "Fast" crystallization			
$T_{\text{T.P.}} = 169.86_4 \pm 0.05°\text{K}$; $A = 0.03846\ \text{deg.}^{-1}$; $N_2^* = 0.03$ mole %[b]			
17.02	5.875	169.8411	169.8229
44.38	2.253	.8498	.8479
66.76	1.498	.8531[a]	.8531
89.13	1.122	.8557[a]	.8557
100.00	1.000		.8566
Pure	0		.8635
B. "Slow" crystallization			
$T_{\text{T.P.}} = 169.86_5 \pm 0.05°\text{K}$; $N_2^* = 0.01$ mole %[b]			
13.62	7.342	169.8495	169.8375
26.93	3.713	.8550	.8508
51.65	1.936	.8576	.8574
70.65	1.415	.8593[a]	.8593
89.61	1.116	.8604[a]	.8604
100.00	1.000		.8608
Pure	0		.8645

[a], [b] See footnotes, Table I.

Curve A in Fig. 5 was determined after the sample had been crystallized by the routine procedure described in paragraph II.B.1. A modified crystallization technique was used before determining curve B. In this experiment the sample was maintained at the melting point with 10% in the liquid phase for 2 days and was then recrystallized slowly over another 2-day period. In all, the sample was in the melting region about four times as long in the second study as in the first.

5. *1-Decene.* — A more striking example of the effects of prolonged "annealing"

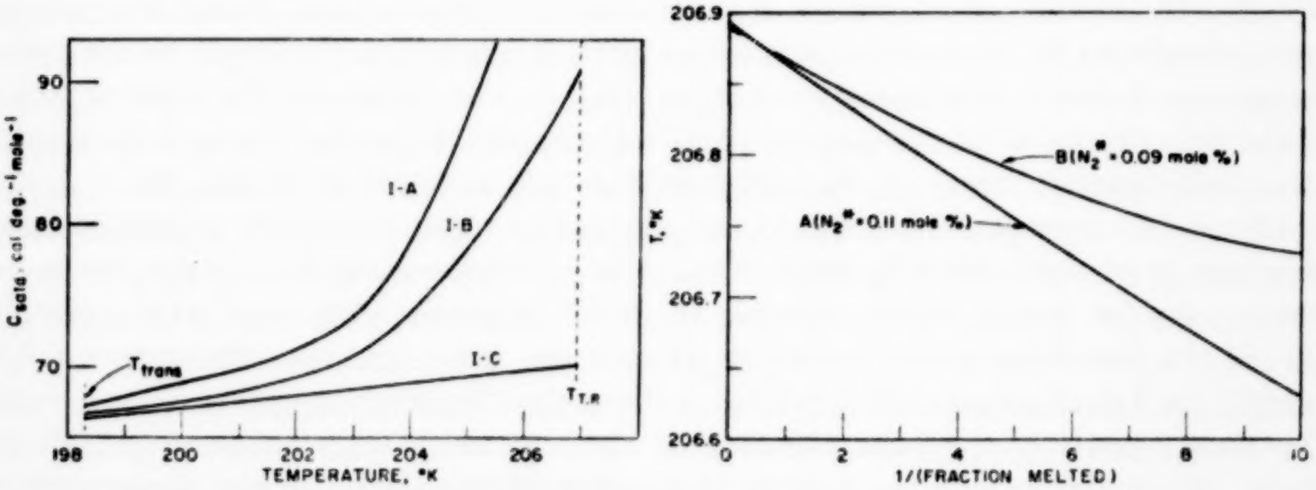

Fig. 6. The heat capacity of 1-decene between the transition-point and triple-point temperatures (6a) and the corresponding melting curves (6b); A, results obtained after relatively "fast" crystallization; B, results obtained after prolonged "annealing" in the premelting region; C, heat-capacity results corrected for premelting.

TABLE VI

1-DECENE: MELTING POINT SUMMARY

Melted, %	1/F	T, °K Obsd.	T, °K Calcd.[b]
A. "Fast" crystallization			
$T_{\text{T.P.}} = 206.89_2 \pm 0.05°\text{K};\ A = 0.03880\ \text{deg.}^{-1};\ N_2^* = 0.11$ mole %[b]			
9.72	10.29	206.6281	206.6045
21.86	4.575	.7662	.7640
42.51	2.352	.8259[a]	.8259
59.10	1.692	.8440	.8444
75.71	1.321	.8547[a]	.8547
100.00	1.000		.8637
Pure	0		.8916
B. "Slow" crystallization			
$T_{\text{T.P.}} = 206.88_9 \pm 0.05°\text{K};\ N_2^* = 0.09$ mole %[b]			
11.04	9.057	206.7373	206.6699
26.45	3.781	.8094	.7974
47.85[c]	2.090	.8397	.8383
51.68	1.935	.8461	.8420
52.31[c]	1.912	.8466	.8426
68.71[c]	1.455	.8497	.8536
71.13	1.406	.8548[a]	.8548
90.56	1.104	.8621[a]	.8621
100.00	1.000		.8646
Pure	0		.8888

[a], [b] See footnotes, Table I.

[c] Single points obtained in the course of separate heat of fusion determinations.

of crystals in the melting or "pre-melting" region is shown by the results for 1-decene[12] in Table VI and Fig. 6. This compound undergoes an isothermal transition about 8° below the melting point, but the transition is easily supercooled. When the sample was crystallized in the routine manner — but not allowed to transpose to the polymorph stable below the transition temperature — the values for the heat capacity of the crystals stable at the melting point fell on curve IA of Fig. 6a, and the results of a melting-point study on the same crystals fell on curve A of Fig. 6b.

In order to transpose 1-decene to the polymorph stable below the transition temperature, it was necessary to hold the sample at temperatures just below the transition point for about 3 weeks. During this time, approximately 0.5% of the sample was in the liquid state as a result of pre-melting. After the low-temperature polymorph had been formed and then heated above the transition temperature to reverse the transformation, the heat capacity of the high-temperature polymorph fell on curve IB of Fig. 6a and the results of a melting-point study on the same crystals fell on curve B of Fig. 6b.

Both heat capacity and both melting curves were obtained reproducibly under the conditions described.

III. DISCUSSION

A. Explanation of anomalous melting curves

The results given in the preceding section for benzotrifluoride, 1-heptanethiol and cycloheptatriene (Figs. 1-3) show that the melting curve of an organic substance can be determined by the calorimetric method with high precision (± 0.0002°) and good reproducibility (± 0.003°). In most cases, the results obtained are in accord with the theory of dilute solutions, either when the impurity is essentially solid-insoluble (Figs. 1 and 2) or is solid-soluble (Fig. 3). Nevertheless, the melting curves obtained for many samples studied in this Laboratory are in some way anomalous.

1. *Sources of error.* — The curves for pyrrole, cyclopentyl-1-thiaethane and 1-decene (Figs. 4-6) are clearly anomalous. Neither the shape of the melting curve in Fig. 4 (curve B) nor the dependence on crystallization procedure shown by the curves in Figs. 4-6 could be predicted by theory. These anomalies may be due to observational errors or to failure to realize the assumed conditions of equilibrium states and ideal solutions. Both observational errors and non-ideal behavior can be eliminated as primary causes of the anomalous melting-point results: The precision of the thermometry is within ± 0.0002° in a single determination and is at least ± 0.0005° in repeated determinations; and departure from ideal behavior should not be a function of the crystallization technique employed. Consequently, it has been concluded that failure to obtain true thermodynamic equilibrium is the cause of anomalies typified by the results in Figs. 4-6.

2. *Pseudo-equilibrium melting curves.* — Nearly all of the samples investigated approached thermal equilibrium by cooling. Although the cooling rate usually becomes 0.00003 deg. min^{-1} or less within an hour after the addition of energy, longer equilibration periods are often encountered. It is possible that equilibration is actually a very slow process requiring many hours or days. A *pseudo*-equilibrium state — not easily recognized as such in the course of experimental observations — might be obtained by two different mechanisms.

First, a *pseudo*-equilibrium state may result from factors inherent in the design of the calorimeter vessel and in the properties of the substances studied. The closely spaced heat-distributing disks and the solid phase of the sample undoubtedly interfere with the diffusion of liquid throughout the vessel. Particularly at low fractions melted, blocked diffusion paths may lead to an inhomogeneous distribution of impurity in the liquid and solid phases. Because the thermal conductivity of organic substances is poor and the process of diffusion is slow, an inhomogeneous distribution of impurity may cause the final approach to thermodynamic equilibrium to occur at an almost undetectable rate. For example, isolated cells containing relatively large amounts of impurity may remain superheated long enough after a fraction is melted that the "final" temperature observed is significantly higher than the equilibrium value. As the fraction of sample in the liquid state increases, isolated cells with high concentration of impurity may be destroyed, and a more homogeneous distribution of impurity may occur. As a result, the values of T_{obsd} at lower fractions melted would be high relative to the more nearly correct values at higher fractions melted. The anomalous melting curve of pyrrole (curve B, Fig. 4) may be explained by this hypothesis. It is believed that inhomogeneous distribution of impurity in the liquid phase may well affect the results of any melting-point determination, although the effect may not be so pronounced as in the example given here.

A second type of *pseudo*-equilibrium melting curve may result as a consequence of non-equilibrium distribution of solid-soluble impurity between the solid and liquid phases. In a comparatively rapid crystallization, differences in the relative rates of deposition of impurity and major component might result in crystals that contain non-equilibrium amounts of impurity in solid-solution. On the other hand, long "annealing" of the crystals near the melting point, with at least some liquid present, provides the opportunity for the impurity to be distributed in equilibrium between the solid and liquid phases.

The dependence on crystallization technique illustrated by the results in Figs. 5 and 6 is consistent with the assumption that non-equilibrium distribution of impurity between solid and liquid phases does occur. It is believed that the melting curves obtained after relatively fast crystallization of cyclopentyl-1-thiaethane and 1-decene (curves A in Figs. 5 and 6b) are lower than those obtained on "annealed" crystals (curves B in Figs. 5 and 6b) because the impurity in the former instances behaved as if it were *less solid-soluble* than in the latter. Curve A in Fig. 6b is as nearly linear as would be expected for a *solid-insoluble* impurity.

It is not possible to decide in every case which of the two proposed mechanisms may be responsible for a *pseudo*-equilibrium melting curve, and in fact, both may operate in a particular determination. For example, it is possible that melting curve B of pyrrole may be higher than "freezing" curve A (Fig. 4) either because of inhomogeneous distribution of impurity or because of differences in the extent of solid-solution formation. However, as will be discussed later (paragraph III.B.2), the anomalous curves for cyclopentyl-1-thiaethane and 1-decene are more likely the result of solid-solution formation.

3. *Evidence from premelting heat capacity data.* — The heat capacity data for 1-decene in the premelting region (Fig. 6a) lend support to the preceding analysis of the observed melting curves (Fig. 6b). The heat capacity values for crystals obtained by more rapid crystallization (curve IA, Fig. 6a) are higher than those for the "annealed" crystals (curve IB, Fig. 6a) because the effect of premelting was larger when the impurity behaved as if it were solid-insoluble. A quantitative test of the explanation offered is afforded by the application of premelting corrections to the heat capacity values. *Upper limits* for the concentration of *effectively solid-insoluble* impurity calculated from the slopes of the melting curves at low fractions melted are 0.09 and 0.05 mole % for curves A and B in Fig. 6b. When heat capacity curves IA and IB are corrected for premelting on the basis of 0.085 and 0.035 mole % solid-insoluble impurity, the results of both determinations fall on a single straight line, curve IC of Fig. 6a.

Evidence obtained in this Laboratory indicates that failure to obtain an equilibrium distribution of impurity throughout the solid phase usually results in *less* than equilibrium concentration. Only one example has been found of the reverse situation — a *greater* than equilibrium concentration of impurity in the solid phase. Like 1-decene, *cis*-decahydronaphthalene[8] undergoes an isothermal transition just below the melting point, and its heat capacity and melting curves are similar in appearance to those given in Fig. 6. In contrast with 1-decene, however, the *higher* melting curve and *lower* heat capacity curve of *cis*-decahydronaphthalene were obtained by the more rapid crystallization procedure. It seems likely that in this case rapid crystallization caused absorption of impurity in solid-solution in greater than equilibrium concentration and that long annealing in the premelting region permitted the impurity to diffuse out of solid-solution. Although only one example of this behavior has been detected, it is reasonable to expect that it may occur fairly often.

B. Limitations of the calorimetric method

Analysis of the results of more than 125 melting-point studies, illustrated by examples in foregoing sections of this paper, has led to a better understanding of the limitations of the calorimetric method. A *pseudo*-equilibrium melting curve may be obtained as a result of inhomogeneous distribution of impurity in the sample or non-equilibrium distribution of impurity between the solid and liquid phases. Such *pseudo*-equilibrium results cannot be recognized easily on the basis of single determinations or even replicate studies ***made in essentially the same way***. For this reason, the interpretation of melting curves is subject to greater uncertainty than was formerly realized.

1. *Uncertainty of impurity values.* — Inhomogeneous distribution of impurity in the liquid phase may result in low values of N_2^* because the slope of the melting curve is usually decreased by this effect (curve B, Fig. 4). However, a more important cause of error is the fairly common formation of solid-solution. For reasons to be discussed later, the methods for treating solid-solution formation are often unreliable in practice. Impurity values reported from this Laboratory have usually been calculated from the slope of the melting curve at high fractions melted by use of eq. (1). If solid-solutions actually are formed, it is evident that the impurity values so calculated will be too low by an unknown and variable factor. The formation of solid-solutions has long been recognized as a possible limitation of all melting-point purity methods, but it has not been realized that the phenomenon is so common. Consequently, it will be worthwhile to consider in more detail the evidence for the assumption that solid-solutions are often encountered in practice.

2. *Evidence of solid-solution formation.* — It is not unreasonable to expect that solid-solutions may be formed in highly purified samples, for the impurities may often be isomeric with the major component and may have nearly the same molecular shape. About half of the melting curves determined in this Laboratory show moderate to pronounced deviation from linearity in plots of T_{obsd} *vs.* $1/F$, indicative of solid-solution formation. Melting curves linear over the entire range of fractions melted (Fig. 1) are rare. If the departure from linearity is slight and primarily at high values of $1/F$ (Fig. 2), it is possible that the observed curvature is due to non-ideal behavior of the more concentrated liquid solutions at low fractions melted or to inhomogeneous distribution of impurity, but it does not seem reasonable to attribute pronounced curvature (Figs. 3, 5 and 6b) to such effects. There are two principal considerations that lead to the conclusion that solid-solution formation often has an important effect on melting-point studies. (1) The results in Figs. 5 and 6 show that melting curves obtained after slow crystallization procedures (the B curves) are higher and depart from linearity *more* than those obtained after relatively fast crystallization (the A curves). Because slow crystallization and pro-

longed annealing before a melting-point study should lead to more nearly equilibrium results, it seems likely that the B curves are "equilibrium" melting curves and are non-linear as a result of solid-solution formation. (2) Comparison of impurity values calculated from heat capacity data in the premelting region with those calculated from melting curves affords strong evidence of solid-solution formation. The heat capacity in the premelting region is extremely sensitive to the presence of impurity, *but only to that which is not in solid-solution.* In this Laboratory, it is the practice to calculate impurity values from premelting heat capacity data as well as from melting curves*. Table VII lists typical results: Values calculated by equation (1) from the slope of the melting curve between $1/F = 1.4$ and $1/F = 1.1$ are given in column 1; values calculated from the slope of the melting curve between $1/F = 10$ and $1/F = 4$ are listed in column 2; and values calculated from premelting heat capacity data are tabulated in column 3. (If the value calculated from melting-point data at *high* values of $1/F$ is significantly lower than that calculated from data at *low* values of $1/F$, the melting curve is appreciably non-linear.) In every instance, the impurity value calculated from premelting data is *less* than or equal to the *lower* of the two values calculated from melting-point data. The heat capacity below the melting point is so sensitive to *solid-insoluble* impurity that the use of the higher impurity values determined from melting curves in calculating premelting corrections would yield "corrected" heat capacity curves of absurd shape. Thus, it is likely that some impurity entered solid-solution in over half of the samples studied in this Laboratory.

TABLE VII

COMPARISON OF IMPURITY VALUES FROM MELTING-POINT AND PREMELTING-HEAT-CAPACITY DATA

Compound[a]	*Impurity, mole %*		
	1[b]	*2*[c]	*3*[d]
1-Heptanethiol	0.04	0.03	0.025
Pyrrole (A)	.015	—	.005
Pyrrole (B)	.006	.006	
Cyclopentyl-1-thiaethane (A)	.03	.01	.005
Cyclopentyl-1-thiaethane (B)	.01	.006	
1-Decene (A & IA)	.11	.09	.085
1-Decene (B & IB)	.09	.05	.035
4,5-Dithiaoctane[8]	.035	.011	.010
Fluorobenzene[8]	.05	.05	.05

[a] The letters A, B, IA and IB refer to the melting and heat capacity curves in Figs. 4-6.
[b] Calculated from the slope of melting curve between $1/F$ values 1.1 and 1.4.
[c] Calculated from the slope of melting curve between $1/F$ values 4 and 10.
[d] Calculated from premelting-heat-capacity data.

3. *Importance of the limitations of melting-point methods.* — Both the formation of solid-solutions and inhomogeneous distribution of impurity will usually cause impurity values calculated from melting-point studies to be too low. The procedure used in this Laboratory — calculation of impurity values from the slope of the melting curve at high fractions melted — will minimize errors in most cases. The results

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* These impurity values are determined for the purpose of correcting observed thermal properties for premelting and usually have not been published as such.

for 1-decene, (Fig. 6b) for example, show that the concentration of impurity calculated as described is not affected significantly by solid-solution formation. On the other hand, it is clear from the results for cyclopentyl-1-thiaethane that solid-solution formation occasionally will cause large percentage errors in calculated impurity values. Study of the results obtained in this Laboratory indicates that as many as 1/3 of the melting curves determined were affected by solid-solution formation to the extent that calculated impurity values were probably 1/2 to 1/10 of the actual value.

4. *The application of solid-solution theory.* — If a melting curve shows evidence of appreciable solid-solution formation, application of a solid-solution treatment[9,10] may give a more accurate impurity value. Unfortunately, the method often has failed to give an adequate representation of observed melting curves — perhaps because measurements were made on a system at *pseudo*-equilibrium or because several impurities were present. In other instances the solid-solution treatment has given an excellent representation of experimental data, but the high sensitivity of the method to small thermometric errors makes the calculated impurity values unreliable. For example, the difference in temperatures observed with 70 and 90% of a sample melted may easily be in error by ± 0.0005°. It can be shown that if the solid-solution treatment is used such an error may correspond to an uncertainty of 500% in the impurity value for very pure compounds with normal cryoscopic constants, whereas the same 0.0005° error corresponds "only" to 150% uncertainty if solid-insolubility is assumed. Thus, unavoidable observational errors may produce such large uncertainty in impurity values calculated by the solid-solution method that values calculated with eq. (1), while obviously low, may be more nearly accurate. For this reason, it has been concluded that the solid-solution treatment is best applied to compounds with low cryoscopic constants (< 0.01 deg.$^{-1}$) or to relatively impure samples (< 99.0 mole %). In such cases, observational errors are likely to be small enough relative to the melting-point depression that they are not important.

5. *Comparison of results by the static and dynamic methods.* — CINES[2] AND MATHIEU[3] have noted that impurity values determined by the calorimetric method in this Laboratory are systematically lower than those determined on the same sample by the dynamic method. Additional evidence based on twice as many comparisons[8] as were available to either CINES or MATHIEU confirms their observation. In most instances, the discrepancy between values of N_2^* obtained by the two methods can be attributed to the lower precision and sensitivity of the dynamic method, particularly if the value of N_2^* is near or less than the normal limit of detection by the dynamic technique. Nevertheless, the calorimetric value of N_2^* may be more in error in some cases as a result of solid-solution formation. The normal crystallization procedure used in this Laboratory often results in at least partial formation of solid-solution. If solid-solution is formed to an appreciable extent, the calorimetric value of N_2^* is likely to be significantly low. The dynamic method, on the other hand, should be affected less by solid-solution formation because the period of observation with this technique is so short that the impurity may not have time to enter solid-solution in equilibrium amounts.

C. *Modification of the calorimetric method*

The two principal limitations of the calorimetric method brought out in the preceding section — that due to inhomogeneous distribution of impurity and that due to the common formation of solid-solutions — probably had a significant effect on at least half the impurity values determined in this Laboratory. Perhaps 1/3 of the impurity values determined are in error by 200% or more. Such errors in impurity are rarely significant if expressed as uncertainty in sample *purity*, but it is worthwhile to consider means for reducing them. Whereas modification of the design of the calorimeter might reduce errors due to inhomogeneity, uncertainties due to solid-solution formation are probably more important and cannot be affected by apparatus changes.

As the results for 1-decene show (Fig. 6b), a solid-soluble impurity can sometimes be made to behave as if it were solid-insoluble by crystallizing the sample rapidly. On the basis of this observation, a modified procedure for melting-point studies is being tested. It is somewhat paradoxical that techniques should be chosen so as to produce *non-equilibrium* results in a classical thermodynamic study. Nevertheless, for purity determinations, more accurate information may often be obtainable from a non-equilibrium melting curve. In the revised procedure, a sample is crystallized as rapidly as possible and observations are begun as soon as *essentially* complete crystallization is obtained. It is hoped that in this way the formation of solid-solution, and resulting errors in N_2^*, can be minimized.

Enough data have not been obtained to determine the utility of the modified procedure, but some advantages and disadvantages of the method are obvious. It is much less time-consuming than the procedure formerly used in this Laboratory — a fortunate circumstance if purity determination is the primary concern — but it is necessary to determine the heat of fusion in separate experiments if an accurate value of this property is desired. If an impurity is forced into solid-solution as in the case of *cis*-decahydronaphthalene, the rapid crystallization technique will give less accuracy than the slow crystallization method. Unfortunately, the modified procedure offers no advantages in many studies because "fast" crystallization is often impossible. In studies that have been made by this method to date, there are indications that inhomogeneity of the liquid phase may be increased and that equilibration times are longer.

However, if the results at high fractions melted are used in calculating impurity values errors due to inhomogeneity should be minimized.

D. Conclusion

The limitations of the calorimetric method for purity determination undoubtedly apply to a greater or lesser extent to any melting-point method. Results such as those discussed in this paper show that uncertainties assigned to impurity values have sometimes been optimistically low. At present, it is not possible to assess the uncertainty that should be assigned to impurity values unless extensive studies are made in each instance of the effect of different operating techniques. In order to obtain quantitative information of general applicability about the effects of the limitations discussed on the results of melting-point studies, further systematic investigations of purity determinations should be made. The following are considered to be fruitful areas for study: (1) The effect of various types and amounts of impurity on the melting curves of samples of known high purity (about 99.999 mole % original purity);

(2) the effect of crystallization and annealing procedures on such known mixtures; and (3) the design of calorimeter vessels especially for use with two-phase systems. A concurrent study of identical samples by the time-temperature method would greatly increase the value of such investigations.

ACKNOWLEDGEMENTS

The work on which this paper is based has been accomplished over the last twelve years and involves the efforts of many of our associates. The late Dr. Hugh M. Huffman, who began these studies, influenced the paper markedly, for his careful experimentation and perceptive analysis of results pointed the way to a better understanding of the calorimetric method. We are indebted also to the following past and present colleagues for their many contributions, both experimental and interpretive: Dr. H. L. Finke, Dr. D. W. Scott, Dr. S. S. Todd, Dr. G. B. Guthrie, Jr., Mrs. M. E. Gross, Mr. J. F. Messerly and Mrs. T. C. Kincheloe.

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SUMMARY

Typical melting curves, chosen from the results of more than 125 melting-point studies, are presented to illustrate both the reliability and the inherent limitations of the calorimetric method of purity determination. It is shown that this method usually is one of the best means of accurately determining small concentrations of impurity. However, analysis of anomalous melting curves leads to the conclusion that *pseudo*-equilibrium curves are often obtained as a result of inhomogeneous distribution of impurity in the liquid phase or of non-equilibrium distribution of impurity between the solid and liquid phases. Evidence is given to support the contention that solid-solutions were formed in as many as half of the samples studied and that for this reason, impurity values calculated for perhaps 1/3 of the samples are in error by 200% or more. Although these large uncertainties in *impurity* values usually correspond to less than 0.1% uncertainty in *purity* values, modified procedures are proposed to minimize such errors.

RÉSUMÉ

Des courbes de fusion typiques, choisies parmi les résultats de plus de 125 études de points de fusion, sont présentées pour illustrer aussi bien la sûreté que les limitations inhérentes de la méthode calorimétrique de détermination de pureté. Les auteurs montrent que cette méthode est généralement l'un des meilleurs moyens de déterminer exactement des petites concentrations d'impureté. Cependant, l'analyse de courbes de fusion anormales amène a conclure que l'on obtient souvent des courbes de pseudo-équilibre dues à une distribution non-homogène d'impureté dans la phase liquide ou d'une distribution d'impureté non-équilibrée entre les phases liquide et solide. Des faits sont présentés qui font supposer que dans la moitié des échantillons étudiés il y aurait eu formation de solutions solides et pour cette raison les teneurs d'impureté calculées pour peut-être un tiers des échantillons seraient fausses de 200% ou davantage. Quoique ces grandes incertitudes des teneurs en impureté correspondent généralement à moins de 0.1% des valeurs de pureté, des procédés sont proposés pour réduire de telles erreurs.

ZUSAMMENFASSUNG

Typische, aus den Ergebnissen von über 125 Schmelzpunkt-Studien gewählte Schmelzkurven werden gezeigt um sowohl die Verlässlichkeit als die inhärenten Begrenzungen der kalorimetrischen Methode zur Reinheitsbestimmung deutlich zu machen. Es wird gezeigt, dass diese Methode meistens eines der besten Mittel ist um niedrige Konzentrationen von Verunreinigungen genau zu bestimmen. Die Analyse abnormaler Schmelzkurven führt aber zu dem Schlusse, dass man oft Pseudo-Gleichgewichts-Kurven erhält, deren Ursache entweder eine nicht homogene Verteilung der Verunreinigung in der flüssigen Phase oder eine nicht dem Gleichgewicht entsprechende Verteilung der Verunreinigung zwischen der festen und flüssigen Phase ist. Es werden Tatsachen angeführt die darauf hinweisen dass vielleicht sogar in der Hälfte der untersuchten Proben feste Lösungen gebildet wurden und dass deshalb die für die Verunreinigung berechneten Werte, in vielleicht 1/3 der Fälle, Fehler von 200% oder mehr aufweisen. Obwohl diese grossen Ungenauigkeiten für die Verunreinigungswerte im allgemeinen einer Ungenauigkeit von weniger als 0.1% für den Reinheitsgrad entsprechen, werden doch abgeänderte Verfahren vorgeschlagen um derartige Fehler zu vermindern.

References p. 96

REFERENCES

[1] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, 35 (1945) 355, and references cited there.

[2] M. R. Cines, *Physical Chemistry of the Hydrocarbons* (edited by A. Farkas), Chapter 8, Academic Press Inc., New York, 1950.

[3] M. P. Mathieu, *Acad. roy. Belg., Classe sci., Mém.*, No. 1639 (1953) 28.

[4] H. M. Huffman, presented at American Chemical Society meeting, New York, September, 1947.

[5] (a) R. A. Ruehrwein and H. M. Huffman, *J. Am. Chem. Soc.*, 65 (1943) 1620; (b) G. D. Oliver, M. Eaton and H. M. Huffman, *ibid.*, 70 (1948) 1502; (c) H. M. Huffman, *Chem. Revs.*, 40 (1947) 1.

[6] H. F. Stimson, *J. Research Natl. Bur. Standards*, 42 (1949) 209.

[7] S. S. Todd, G. D. Oliver and H. M. Huffman, *J. Am. Chem. Soc.*, 69 (1947) 1519.

[8] Unpublished results, this Laboratory.

[9] H. L. Finke, presented at the Seventh Annual Calorimetry Conference, Washington, D. C., September, 1952.

[10] S. V. R. Mastrangelo and R. W. Dornte, *J. Am. Chem. Soc.*, 77 (1955) 6200.

[11] H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly and Guy Waddington, *J. Am. Chem. Soc.*, 78 (1956) 5469.

[12] J. P. McCullough, H. L. Finke, M. E. Gross, J. F. Messerly and Guy Waddington, *J. Phys. Chem.*, 61 (1957).

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THERMAL ANALYSIS OF NORMAL ALKANES

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I. INTRODUCTION

In principle the determination of the purity of a certain compound by thermal analysis is simple if it is known what impurity is present and if the heat of fusion of the component or of the component and of the "impurity" is also known. In an ideal case Raoult's equation can be applied.

It has been found, however, that this determination is sometimes not possible without a complete knowledge of the binary system of the compound under investigation with its impurity, or even of that of a multi-component system containing several admixtures.

A few examples which have been encountered in the study of mixtures of pure normal alkanes will be dealt with.

II. EXPERIMENTAL PART

The heating curves — temperature *versus* number of calories supplied to the sample — were obtained in two different ways.

1) A small silver vessel, filled with gold plated nickel gauze*, which contains about one gram of substance, was used. The silver vessel was placed in the centre of a heavy hollow copper sphere which could be heated electrically from the outside. The temperature difference between the inner wall of the copper bulb and the middle of the silver vessel was kept constant automatically. The temperature in the middle of the sample was recorded with an accuracy of ± 0.05°C. The heat flow to the silver vessel was determined for each temperature range of 5°C and various temperatures differentials; it was almost constant for a particular differential in the range between 20° and 80°C.
   With pure compounds a very sharp break was obtained between the heating-up curve of the solid phase and the beginning of the melting process; the break between the end of melting and the beginning of heating-up the liquid was also quite sharp. With about one gram of substance the melting process took about 30 minutes under the circumstances chosen for the experiment; the temperature difference of the sample between the beginning of the melting process and its end was usually not more than 0.2°C.
2) A sample of about 250 mg was spread out in a very thin layer** between two concentric cylindrical vessels, the inner of which was of silver. The temperature of the sample was accurately measured (to 0.01°C) every minute. The sample was heated by keeping the temperature difference between a brass block in which the vessels were placed (with an intermediate air space) and the sample constant. In this case hand regulation was employed.
   The breaks in the curves at the end of the two-phase transitions in the pure compounds were about as sharp with method 2 as with method 1.

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* STRAUB AND MALOTAUX[1] first described the use of such a silver vessel, with manual operation. The present modification of this apparatus, with fully automatic control, was developed in the Koninklijke/Shell-Laboratorium, Amsterdam.

** Apparatus comparable with that of SMIT[2].

III. BINARY SYSTEMS OF SOME *n*-ALKANES

Limiting ourselves to the thermal analysis of binary systems of *n*-alkanes, we have to find out in the first place, whether the two components constitute an eutectic mixture or if mixed crystals are formed. The following types of systems, already described by BAKHUIS ROOZEBOOM[3] are possible (see Fig. 1).

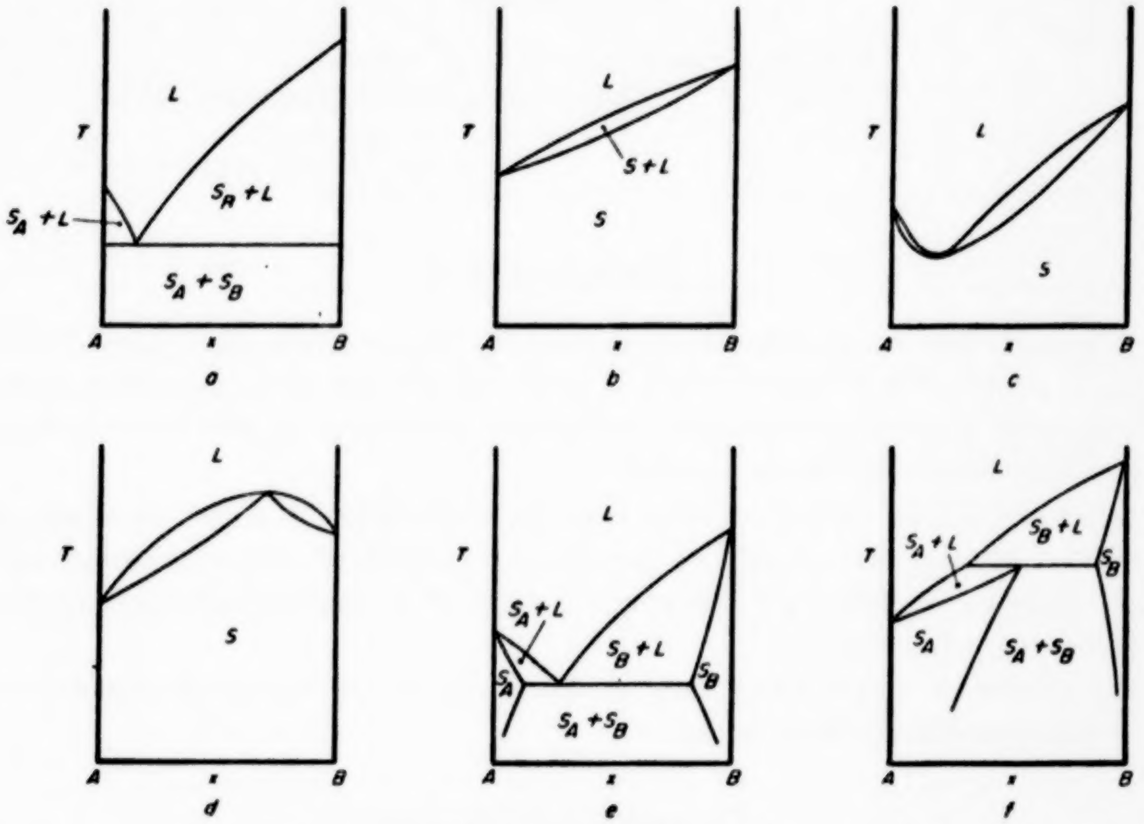

Fig. 1. Some possible T-x diagrams of binary systems.

In the case of Fig. 1a the components are completely immiscible in the solid state and form a eutectic mixture. In the cases of Figs. 1, b, c, d the components are completely miscible both in the liquid and the solid state. The solid-liquid equilibria in cases 1, c and d show a minimum and a maximum respectively, a fact pointing to a less ideal behaviour of the components. In Figs. 1, e and f the temperature-composition diagram is given for complete miscibility in the liquid state but only partial miscibility in the solid phase.

The calculation of the solid-liquid equilibria in the systems 1, a and b is quite simple. In the cases of Fig. 1, c, d, e and f there is no general expression for the composition of either the liquid and solid phase as a function of the temperature. Approximations for the shape of at least a part of these curves can however be derived.

a) The first two types of curves (Fig. 1, a and b) have been employed by the present author[4] for mixtures of n-$C_{21}H_{44}$ — n-$C_{31}H_{64}$ (Fig. 2, case of Fig. 1, a) and n-$C_{21}H_{44}$ — n-$C_{23}H_{48}$ (Fig. 3, case of Fig. 1, b) respectively.

The latter heating curves are simple and easy to interpret, they leave no room for uncertainties. The amount of "impurity" — in this case the amount of the second component — can be calculated with sufficient accuracy.

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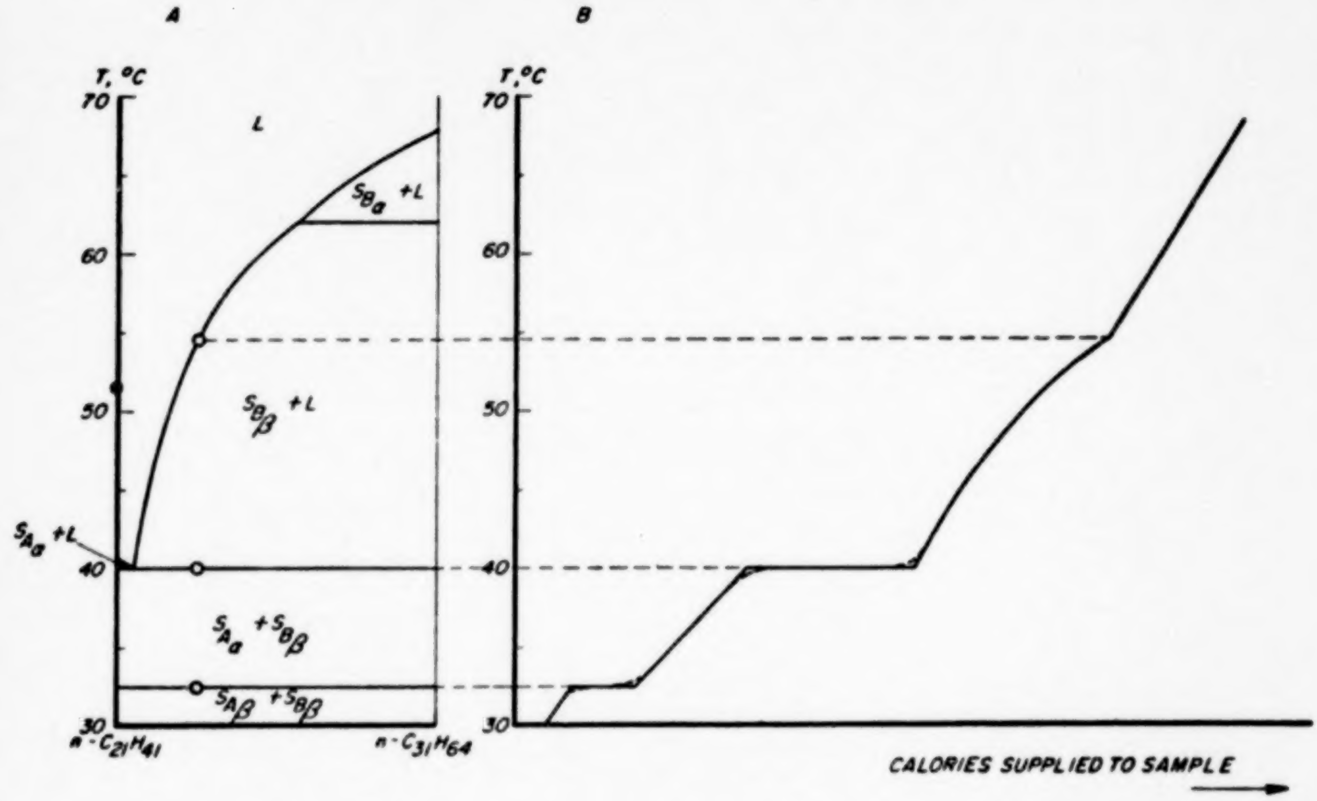

Fig. 2. A. *T-x* diagram of mixtures of *n*-$C_{21}H_{44}$ and *n*-$C_{31}H_{64}$.
B. Heating curve for 75 mol% *n*-$C_{21}H_{44}$ and 25 mol% *n*-$C_{31}H_{64}$.

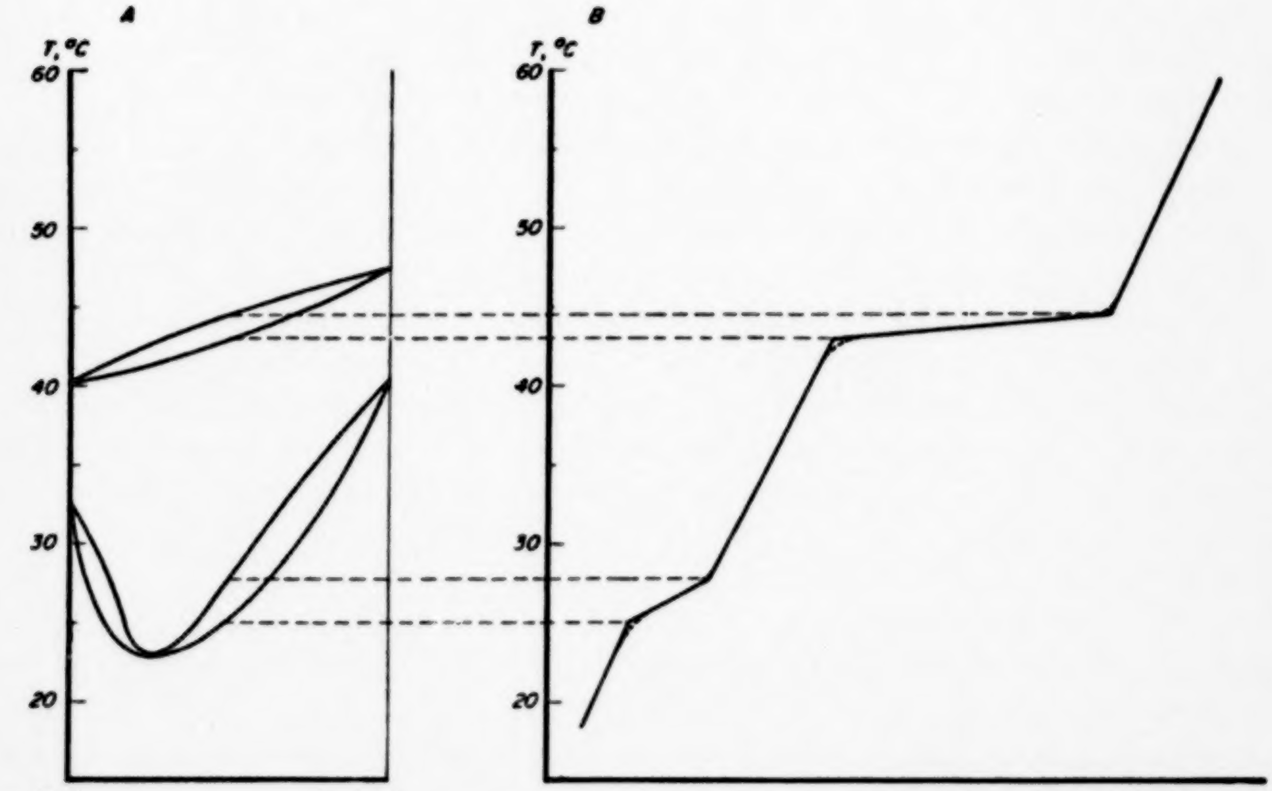

Fig. 3. A. *T-x* diagram of mixtures of *n*-$C_{21}H_{44}$ and *n*-$C_{23}H_{48}$.
B. Heating curve for 50 mol% *n*-$C_{21}H_{44}$ and 50 mol% *n*-$C_{23}H_{48}$.

The purity of the components of these systems was checked by mass spectrometry; they were found to be pure to the limit of the resolution of the instrument, *i.e.* to over 99.9%.

b) Another case of thermal analysis of *n*-alkanes is given in Fig. 4, A and B.

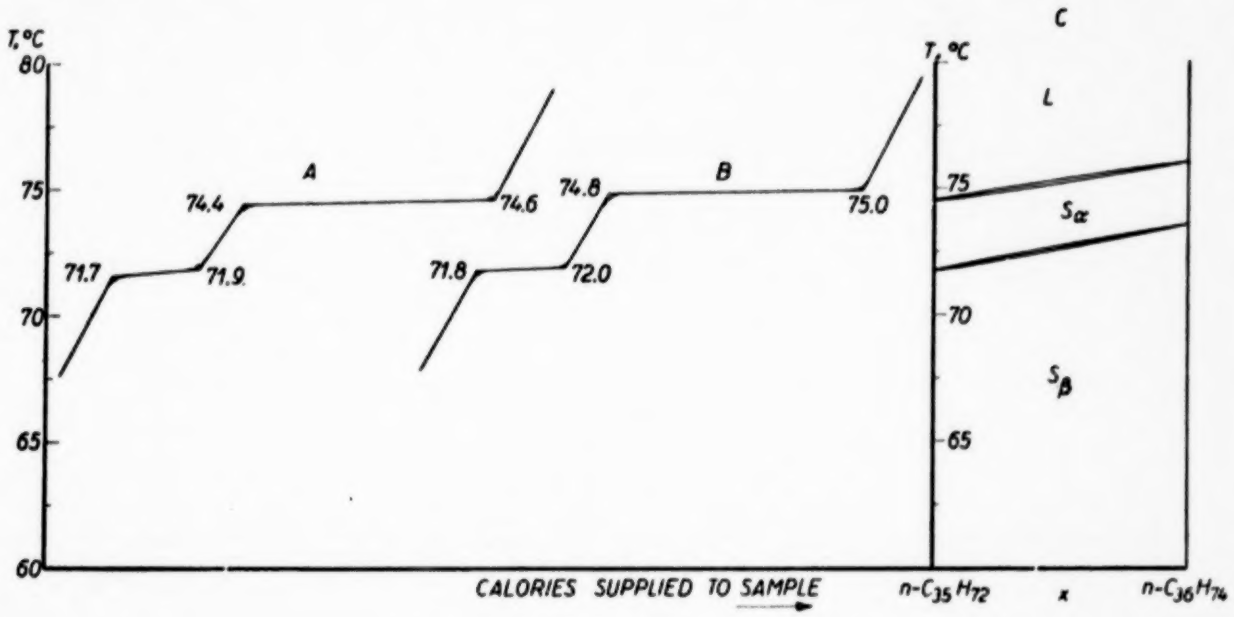

Fig. 4. A. Heating curve for pure n-$C_{35}H_{72}$.
B. Heating curve for 75 mol% n-$C_{35}H_{72}$ and 25 mol% n-$C_{36}H_{74}$.
C. *T*-*x* diagram of mixtures of n-$C_{35}H_{72}$ and n-$C_{36}H_{74}$.

Comparing the two parts A and B of the figure, one finds that in both cases a transition point in the crystalline state is present, which in the case of Fig. 4 A runs from 71.7 to 71.9°C and in the case of Fig. 4 B from 71.8 to 72.0°C. The melting points run from 74.4 to 74.6°C and from 74.8 to 75.0°C respectively. The slope of the curves representing the two-phase transitions is what could be expected from the behaviour of a pure substance: the breaks in the curves between the heating-up of the solid β phase (stable at low temperatures) and the transition into the α phase, between the transition and the heating-up of the α phase, between the heating-up of the α phase and melting, and between melting and the heating-up of the liquid is in all cases sharp; differences in these respects are not visible between Fig. 4 A and 4 B, one would be inclined to believe that in both cases a pure compound was involved. However, Fig. 4 A represents the heating curve of really pure pentatriacontane (n-$C_{35}H_{72}$), whereas Fig. 4 B shows the heating curve of a mixture of 75 mol% of pentatriacontane and 25 mol% of hexatriacontane (n-$C_{36}H_{74}$).

Further investigation of the binary system revealed that the two components form a continuous range of mixed crystals; the *T*-*x* diagram has the shape of Fig. 4 C. The solid-liquid equilibrium as well as the solid α - solid β equilibrium have a very narrow range of coexistance.

As 25 mol% of n-$C_{36}H_{74}$ admixed with n-$C_{35}H_{72}$ raises its transition point by only 0.1°C and the melting point by 0.4°C, it would in practice not have been possible to detect a small percentage of hexatriacontane in pentatriacontane, since no other differences in the shape of the curves reveal the presence of an "impurity".

c) An interesting comparison can be made between the behaviour of pure *n*-octadecane (n-$C_{18}H_{38}$) with that observed for this alkane in the presence of small quantities of other hydrocarbons.

UBBELOHDE[5] has described the behaviour of what he believed to be a pure sample of this compound. From the curve representing the specific heat as a function of the temperature he came to the conclusion that the alkane shows "premelting" to about 15°C below its point of fusion. He stated that this "premelting" is not due to the formation of liquid in crevices of the solid, but appears to be the result of a process taking place within the solid phase in the neighbourhood of the melting point.

The somewhat vague indications given by UBBELOHDE can be fully understood by studying the complete binary systems of n-$C_{18}H_{38}$ with other normal alkanes. It should be remarked, however, that not only melting and/or setting points have to be determined as was done by UBBELOHDE, but that the behaviour in the solid state has also to be studied in order to understand the behaviour of this hydrocarbon in mixtures with other alkanes.

Really pure octadecane, the purity of which was again checked by mass spectrometry, was found by the writer not to show any abnormal behaviour upon heating. No transitions in the solid state occur.

Binary systems of octadecane with n-heptadecane or with n-hexadecane were then studied. The behaviour of the system n-$C_{18}H_{38}$ — n-$C_{17}H_{36}$ will be described in some detail.

Fig. 5 shows the heating curve for a mixture of 80.9 mol% of n-$C_{18}H_{38}$ and 19.1 mol% of n-$C_{17}H_{36}$. A very simple curve is obtained, which clearly indicates a transition range from 19.8° to 23.5°C where one crystal modification is transformed into another, and a melting range from 26.0 to 26.4°C.

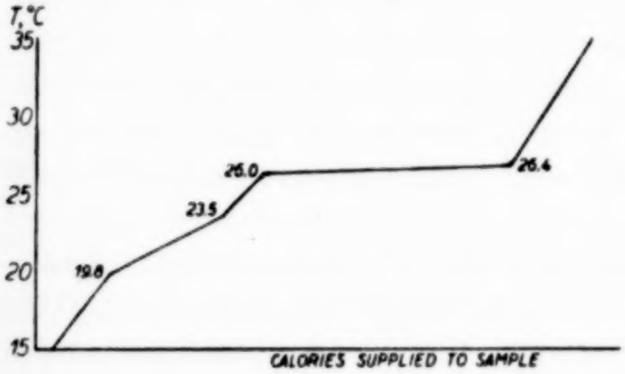

Fig. 5. Heating curve for 80.9 mol% $C_{18}H_{38}$ and 19.1 mol% $C_{17}H_{36}$.

A much more complicated behaviour is shown in Figs. 6 and 7, which give the heating curves of mixtures containing 88.5 and 92.9 mol% of $C_{18}H_{38}$ respectively.

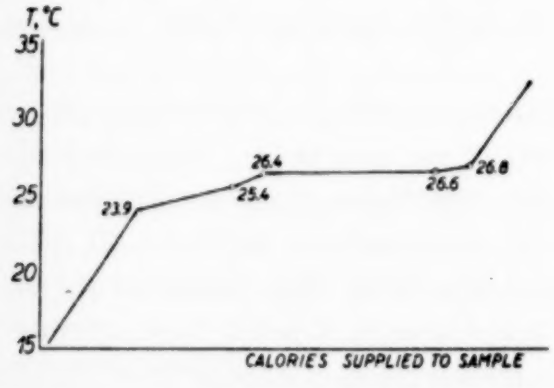

Fig. 6. Heating curve for 88.5 mol% $C_{18}H_{38}$ and 11.5 mol% $C_{17}H_{36}$.

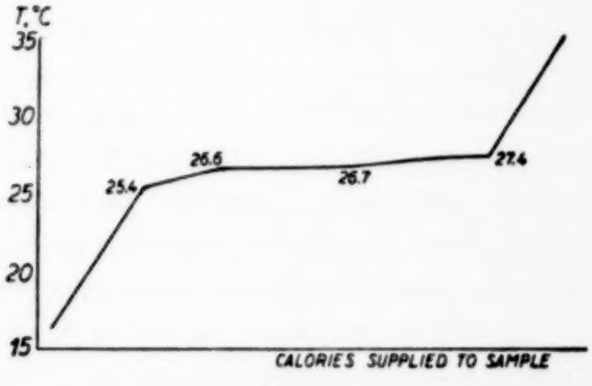

Fig. 7. Heating curve for 92.9 mol% $C_{18}H_{38}$ and 7.1 mol% $C_{17}H_{36}$.

Without further knowledge of the complete binary system it is almost impossible to explain these curves and it would be completely impossible to calculate impurities from their shape.

Other mixtures of the two alkanes were also studied. In view of the scope of the present symposium it is not necessary to give full details of the behaviour of all these mixtures. It should be mentioned, however, that a mixture containing 97.5 mol% of n-$C_{18}H_{38}$ did not show any transition phenomena; a heating curve was obtained which in principle had the same shape as that of pure octadecane, the only difference being that no constant melting point was observed, but instead a melting range from 27.7 to 28.1°C. Since the pure octadecane shows a monotropic behaviour (it has a metastable melting point at 27.5°C), it is obvious that also the mixtures with compositions close to the pure component should be monotropic. In other words, on the extreme right of the binary T-x diagram, near to the axis of octadecane, only one stable modification S_β exists, which upon heating transforms into a liquid via the melting range ($S_\beta + L$, Fig. 8).

The mixtures on the left side, however, are enantiotropic, because n-heptadecane shows enantiotropy. Consequently a change from the one type into the other must take place somewhere in between. Such a change can only occur via a three-phase equilibrium, represented in Fig. 8 by the horizontal line S_β — S_a — L. Since all three phases are in equilibrium at this temperature, all two-phase equilibria are also involved. Hence all two-phase areas will intersect the three-phase line.

The three-phase equilibrium can easily be recognized from heating curves since relatively large heat effects are involved. Since the heat of a three-phase equilibrium is set free or taken up at constant temperature, the cooling or heating curves must show a horizontal part. However, as in the case of pure compounds (which should have a perfectly level step at two-phase equilibria, but always undergo a small rise in temperature there), the curves never show a completely constant temperature from start to finish. The differences in temperature between the beginning and the end of the transformation are, however, very small and of the order of magnitude of 0.1 to 0.3°C at most.

The heating curves of Figs. 6 and 7 can now easily be understood from the phase diagram (T-x) in Fig. 8. The heating curve at a composition of 88.5 mol% of $C_{18}H_{38}$ (Fig. 6) shows a transition range from 23.9 to 25.4°C, then the heating-up of the a modification occurs, from 25.4 to 26.4°C; melting of this modification starts at 26.4°C and continues until the three-phase equilibrium is reached at 26.6°C, where the transformation $S_a \rightarrow S_\beta + L$ takes place and continues until the S_a phase has been converted completely into the others. From 26.6 to 26.8°C melting of the S_β phase takes place.

The heating curve in Fig. 7 of a mixture containing 92.9 mol% octadecane can be explained as follows. A transition from the S_β crystal phase into the S_a crystal phase proceeds from 25.4 to 26.6°C, at which temperature the three-phase equilibrium is reached. Here again the transformation $S_a \rightarrow S_\beta + L$ occurs, up to about 26.7°C, where S_a phase seems to have completely disappeared; from this temperature on melting of the S_β phase occurs until at 27.4°C the last traces of solid have become liquid.

An analogous behaviour is found in the system n-octadecane — n-hexadecane, with the difference, however, that n-hexadecane is also monotropic as a pure component. A three-phase equilibrium is now observed on both sides of the *T*-*x* diagram (Fig. 9).

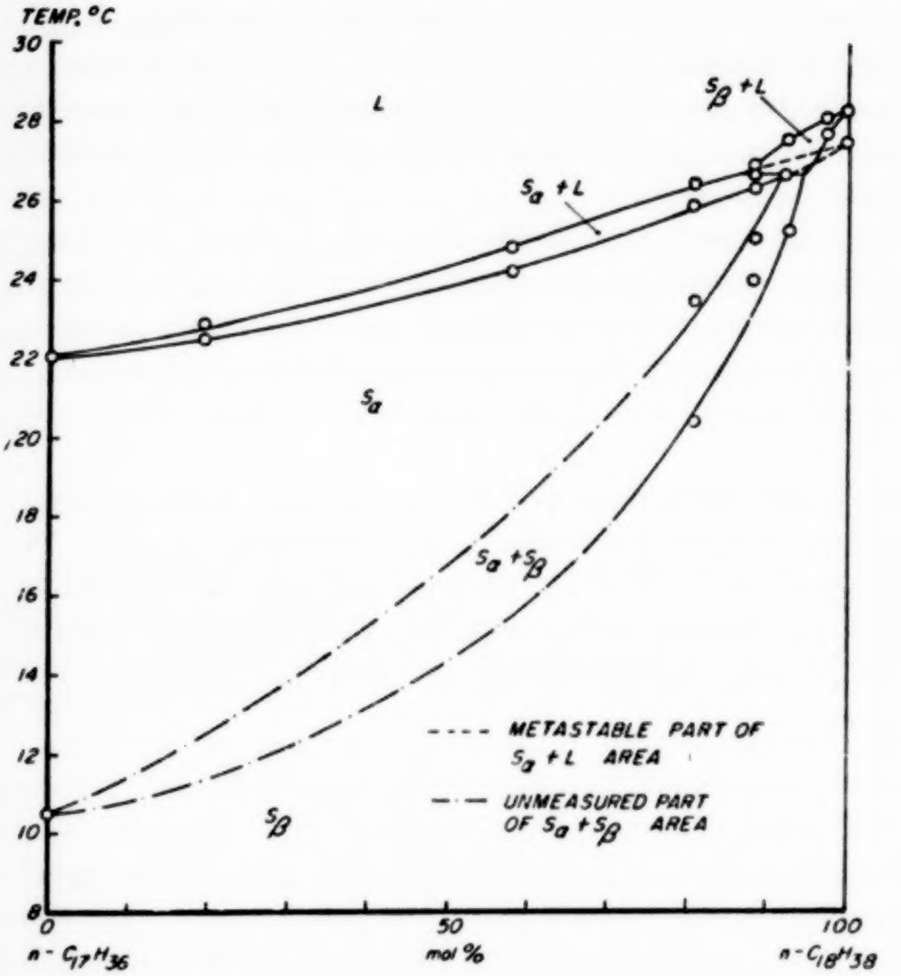

Fig. 8. System n-$C_{17}H_{36}$—n-$C_{18}H_{38}$.

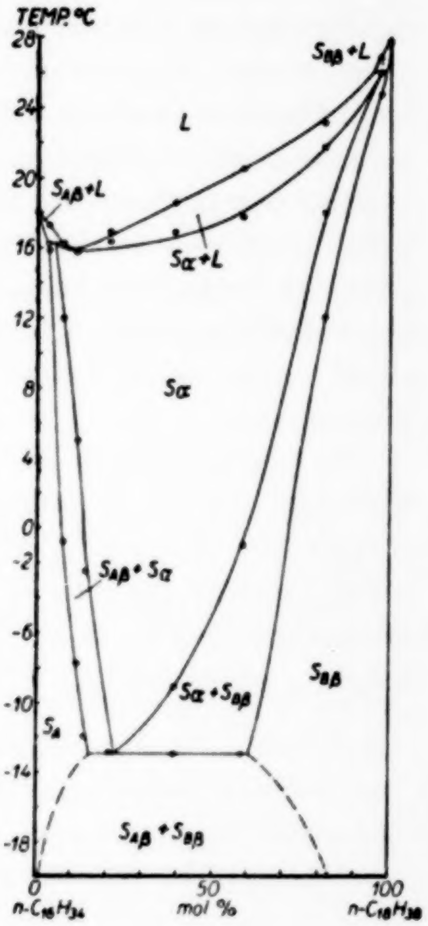

Fig. 9.
System n-$C_{16}H_{34}$—n-$C_{18}H_{38}$.

Moreover, the three-phase lines have shifted somewhat nearer to the axes of the pure components, so that a smaller percentage of the other component gives rise to the complicated behaviour described for the previous binary system. Returning now to the behaviour of the "pure" octadecane described by UBBELOHDE, it can be seen from the melting point of his substance (27°C) and from the fact that his octadecane shows transition phenomena that it must have been by no means a pure compound. If the impurity was only *n*-hexadecane, one would estimate from Fig. 9 an amount of about 3 mol%; if it was, however, heptadecane the amount of this compound can be estimated from Fig. 8 as being about 10 mol%. As the type of impurity or impurities is not known and as the study of more complicated systems in our investigations has not been concluded, an exact estimate cannot be given.

A few other conclusions can, however, be drawn. Pure octadecane does not show a transition in the solid state. Impurities in the form of other *n*-alkanes introduce a transition; the mixture behaves like an enantiotropic substance. The phenomena observed by UBBELOHDE might be ascribed to the transition of $S_{B\beta}$ crystals into S_α crystals. UBBELOHDE's X-ray measurements on mixtures of *n*-hexadecane and *n*-octadecane in a certain range of concentration show the simultaneous presence of what he terms "standard octadecane", which was a preparation of lower purity, and his so-called "pure octane". Possibly the range in question will have been the two-phase area

$S_{B\beta} + S_\alpha$ of Fig. 9. Very probably only one crystal structure will be found in the whole $S_{B\beta}$ area alongside pure octadecane. If X-ray photographs are to be taken in such case, however, it will be necessary to keep the temperature very closely constant, as a small change may lead to a transformation into another crystal type (Figs. 8, 9).
d) The author has observed similar phenomena as described for the *n*-octadecane in other binary systems of *n*-alkanes. In these cases the determination of the purity from thermal analysis will again be a matter of great difficulty if the complete behaviour of the binary system is not known.

Only one further example need be given here. *n*-Eicosane ($C_{20}H_{42}$) has a melting point of 36.5°C and does not show any transition point if the compound is absolutely pure. Its heating curve has the general shape of that of a pure substance only possessing a melting point. Mixtures with small quantities of other *n*-alkanes, with a molecular weight either below or above that of *n*-eicosane, however, do show transition phenomena.

The explanation is the same as for the binary systems containing *n*-octadecane. This fact will be illustrated for the system *n*-eicosane — *n*-nonadecane ($C_{19}H_{40}$). A mixture of 95.8 mol% of *n*-eicosane and 4.2 mol% of *n*-nonadecane clearly shows a temperature (35.2 to 35.5°C) in the heating curve (Fig. 10), where the three-phase transformation $S_\alpha \rightarrow S_\beta + L$ takes place. At higher temperatures (35.8 to 36.0°C) the solid S_β phase melts.

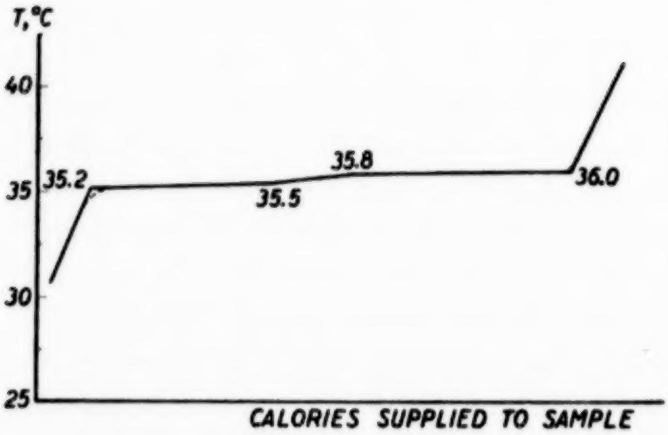

Fig. 10. Heating curve for 95.8 mol% $C_{20}H_{42}$ and 4.2 mol% $C_{19}H_{40}$.

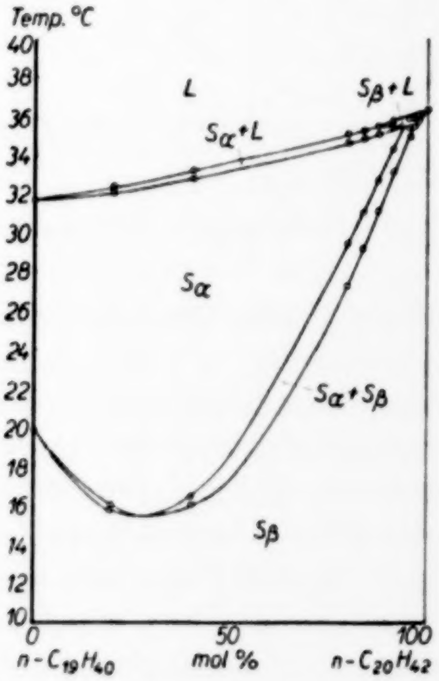

Fig. 11. System n-$C_{19}H_{40}$ — n-$C_{20}H_{42}$.

Mixtures with 3.7 mol% of nonadecane give a heating curve that cannot be interpreted with certainty. Even with an insight into the binary system it is impossible to see if we pass the three-phase equilibrium or not (Fig. 11).

Compositions with a still smaller amount of nonadecane definitely show only one melting range. This behaviour can easily be understood from the binary *T*-*x* diagram (Fig. 11). The $S_\alpha + S_\beta$ area descends much more steeply to lower temperatures if alkanes with molecular weights higher than that of *n*-eicosane are taken as second component. Moreover, the area in these cases, at a concentration eicosane. It is quite normal to find a transition area lies closer to the axis of the pure of about 3% of the second component, which descends below the three-phase equilibrium to the extent of 12 to 24°C, depending upon the molecular weight of the second component. It is quite clear that heating curves are very difficult to interpret in these cases and that it is impossible to calculate "impurities" from the curves alone.

e) It was moreover very often found upon cooling, when the curve crosses melting and transition areas, that crystals of divergent compositions are formed. The heating curves obtained immediately after cooling, or even a couple of days after cooling, were as a consequence unreliable and quite different from the curves obtained on mixtures which were considered to be in equilibrium. The samples regained their homogeneity after storage for several days or weeks, as a result of recrystallization.

IV. FINAL REMARKS

In this paper a survey has been given of some phenomena which can occur in binary systems of normal alkanes. Their behaviour, which is frequently complicated, makes it difficult to use the thermal analysis of these alkanes as a means of determining impurities.

Although no other systems than *n*-alkane mixtures were investigated, it is quite possible that analogous difficulties can occur with other compounds, such as long-chain alcohols, fatty acids or esters. In such cases it is therefore recommended to study the complete binary system in question, or even multi-component systems, in order to avoid arriving at wrong conclusions as regards the amount of "impurity" present in the compound under investigation.

ACKNOWLEDGEMENT

The writer thanks several of his fellow-workers for assistance rendered in this investigation and the management of the Koninklijke/Shell-Laboratorium, Amsterdam for permission to publish the above results.

SUMMARY

The thermal analysis of *n*-alkanes and their mixtures has shown that a complicated binary system sometimes exists. This fact makes it difficult to interpret the heating curves; in certain cases it will not be possible to calculate from these curves in a simple manner the amount of a second component present in a given alkane. A complete insight into the behaviour of the binary system will then be necessary in order to interpret the heating curve and to estimate the amount of "impurity" accompanying a particular alkane. Multi-component systems may even have to be studied if more than one "impurity" is present.

RÉSUMÉ

L'analyse thermique des *n*-alcanes et de leurs mélanges a montré qu'un système binaire compliqué existe parfois. Ce fait rend difficile l'interprétation des courbes de chauffage; dans certains cas il ne sera pas possible de calculer, à partir de ces courbes, d'une manière simple, la quantité d'un second composant présent dans un alcane donné. Une connaissance complète du comportement du système binaire sera alors nécessaire afin de pouvoir interpréter la courbe de chauffage et d'évaluer la quantité ,,d'impureté'' accompagnant un alcane particulier. Pour les systèmes à plusieurs composantes une étude peut même être nécessaire si plus d'une ,,impureté'' est présente.

ZUSAMMENFASSUNG

Die thermische Analyse von *n*-Alkanen und ihren Gemischen hat gezeigt, dass manchmal ein kompliziertes binäres System vorliegt. Diese Tatsache macht die Interpretierung der Erhitzungskurven schwierig; in gewissen Fällen wird es nicht möglich sein aus diesen Kurven auf einfache Weise die Menge eines zweiten in einem gegebenen Alkan vorhandenen Bestandteiles zu berechnen. Eine vollständige Einsicht in das Verhalten des binären Systems wird dann nötig sein, um die Erhitzungskurve zu interpretieren und die Menge einer, ein bestimmtes Alkan begleitenden ,,Verunreinigung'' zu berechnen. Bei Systemen mit mehreren Komponenten kann sogar eine Untersuchung nötig sein, wenn mehr als eine ,,Verunreinigung'' vorhanden ist.

REFERENCES

1 J. Straub and R. N. M. A. Malotaux, *Rec. trav. chim.*, 52 (1933) 275.
2 W. M. Smit, *Chem. Weekblad*, 36 (1939) 750; *Rec. trav. chim.*, 75 (1956) 1309.
3 H. W. Bakhuis Roozeboom, *Z. physik. Chem.*, 30 (1899) 385, 413.
4 W. M. Mazee, *J. Inst. Petroleum*, 35 (1949) 97.
5 A. R. Ubbelohde, *Trans. Faraday Soc.*, 34 (1938) 292.

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FREEZING POINT AND HEATING CURVE BEHAVIOR FOR AN ORGANIC RECIPROCAL SALT PAIR SYSTEM

by

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INTRODUCTION

In the course of an investigation of methods of separating and purifying homologous long chain fatty acids it became necessary to obtain fundamental information on the freezing points of binary mixtures of certain amine salts. The present paper deals with the explanation of the seemingly anomalous freezing point and heating curve behavior in some of these systems.

EXPERIMENTAL PROCEDURE

Pure cyclohexylamine stearate (CS), cyclohexylamine palmitate (CP), 2,2′-dipyridylamine stearate (DS), and 2,2′-dipyridylamine palmitate (DP) were prepared by mixing equimolar amounts of the amine and the acid and recrystallizing repeatedly from a solvent until there was no change in the freezing point. All recrystallizations were performed from concentrated solutions in centrifugal filtration tubes[1]. The samples were dried in a vacuum over solid potassium hydroxide and had the following freezing points and nitrogen analyses: CS, f.p., 93.0°C; N, 3.58%, theory 3.65%; CP, f.p., 90.6°C; N, 3.93%, theory 3.94%; DS, f.p., 66.3°C; N, 9.19%, theory 9.22%; and DP, f.p., 60.8°C; N, 9.87%, theory 9.83%. It was found that the fatty acids regenerated from these salts had been freed from homologous acids[2].

The freezing point determinations were made by the thermostatic, sealed-tube method[3], which involves finding two temperatures a few tenths of a degree apart, at one of which liquefaction is complete and at the other a few crystals persist after a long period of agitation at constant temperature. The heating curves were obtained by a procedure previously described[4]. The 0.5 to 0.7 gram sample was sealed in a thin glass tube supplied with a thermocouple well and was suspended in an air space surrounded by a shield, the temperature of which was raised at a constant rate of about 0.1°C per minute. The temperatures of the melt and the shield were followed by single junction copper-constantan thermocouples, readings being made to the nearest microvolt.

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* One of the laboratories of the *Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.*

TABLE I

FREEZING POINT DATA FOR BINARY AND QUASI-BINARY SYSTEMS

Mole % of A^{a}	*Freezing point °C*	*Mole % of A*^{a}	*Freezing point °C*	*Mole % of A*^{a}	*Freezing point °C*
CP-CS System^{b}		DS-CS System^{b}		DP-CP System^{b}	
0.00	93.0	0.00	93.0	0.00	90.6
11.01	90.7	15.29	88.3	15.03	85.2
20.40	88.6	24.67	84.5	25.02	80.3
29.79	86.1	39.82	78.5	40.50	73.2
39.90	83.2	49.35	75.0	49.32	69.5
51.28	79.9	61.94	69.8	62.90	63.7
53.4^{c}	79.4^{c}	68.89	66.8	70.24	60.2
59.58	81.0	74.89	64.0	75.45	58.2
69.79	83.5	75.7^{c}	63.6^{c}	75.6^{c}	57.9^{c}
79.74	85.7	79.50	64.3	79.16	58.4
88.48	88.0	84.21	64.9	85.17	59.3
100.00	90.6	89.47	65.6	89.46	59.6
		100.00	66.3	100.00	60.8
DP-DS System^{b}		DS-CP System^{b}		DP-CS System^{b}	
0.00	66.3	0.00	90.6	0.00	93.0
15.37	64.1	10.24	85.0	10.59	87.6
25.03	63.0	23.63	75.4	21.32	81.3
39.94	59.6	30.02	70.7	29.98	75.8
49.86	57.2	39.72	64.1	39.85	70.0
54.60	56.0 (55.2)	41.4^{c}	62.9^{c}	46.21	65.7
59.80	54.8	44.96	63.1	50.44	63.1
62.8^{c}	53.8^{c}	49.69	63.2	55.07	59.8
64.54	54.4	53.80	62.8	60.7^{c}	55.9^{c}
70.25	55.2	59.20	62.3	65.14	55.2
73.76	55.8 (55.0)	68.84	60.7	69.93	54.0
79.24	57.4	72.8^{c}	59.6^{c}	71.65	53.8
89.49	59.2	79.77	61.6	73.6$_{c}$	53.1^{c}
100.00	60.8	88.63	63.9	75.21	53.8
		100.00	66.3	79.33	54.9(51.3)^{d}
				89.23	58.2
				100.00	60.8
DP-Mixture *a* System^{b}		Mixture *b*-Mixture *a* System^{b}		CP-Mixture *c* System^{b}	
0.00	78.7^{e}	0.00	78.7^{e}	0.00	57.3^{e}
43.68	58.8	55.07	54.4	23.55	52.4
53.12	53.8	59.0^{c}	52.0^{c}	26.53	51.9
54.9^{c}	52.5^{c}	59.03	52.0	27.1^{c}	51.7^{c}
54.90	52.5	59.93	52.0	27.47	51.9
58.15	52.5	61.84	52.0	29.65	53.0
62.08	52.7	63.31	52.0	100.00	90.6
64.47	52.6	67.24	52.0		
68.13	52.6	69.0^{c}	51.8^{c}	CP-Mixture *d* System^{b}	
68.2^{c}	52.5^{c}	70.59	(51.8)^{d}		
69.63	(52.5)^{d}	72.77	(51.6)^{d}	0.00	56.2^{e}
72.14	(52.3)^{d}	78.55	55.2	24.12	52.2
77.71	55.6 (51.6)^{d}	83.32	56.1	25.92	51.8
100.00	60.8	100.00	59.9^{e}	26.7^{c}	51.7^{c}
				28.83	52.9
				100.00	90.6

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[a] A is first-mentioned substance.

[b] CP = cyclohexylamine palmitate; CS = cyclohexylamine stearate;
DP = 2,2′-dipyridylamine palmitate; DS = 2,2′-dipyridylamine stearate;
Mixture *a* = 60% CS—40% DS; Mixture *b* = 92% DP—8% CP;
Mixture *c* = 50% DS—50% DP; and Mixture *d* = 46% DS—54% DP.

[c] Eutectic or peritectic by graphical interpolation.

[d] Parenthetical values are metastable equilibria.

[e] Graphical interpolation.

FREEZING POINT MEASUREMENTS

The freezing point data for the binary systems CS-CP, DS-DP, CS-DS, CP-DP, CS-DP, and DS-CP are given in Table I and shown graphically in Fig. 1. The first four systems are of the simple eutectic type. The shape of the freezing point diagrams

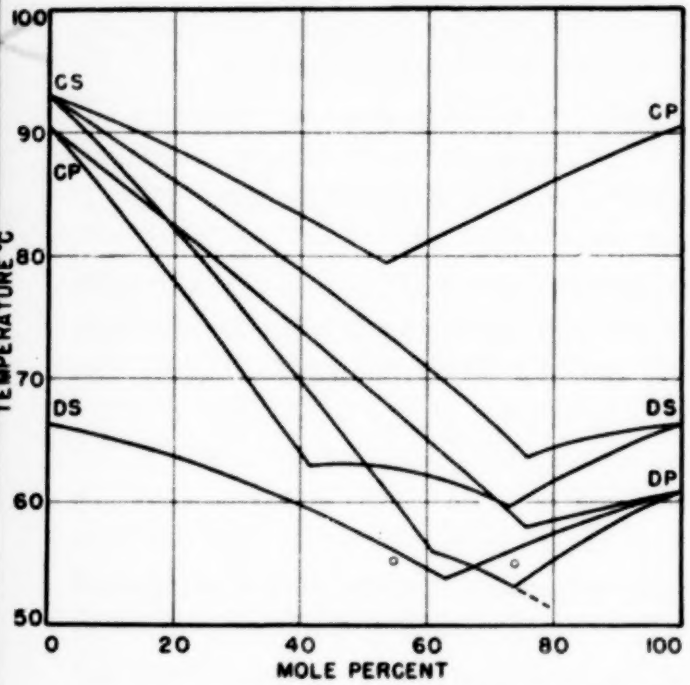

Fig. 1. Binary and quasi-binary freezing point diagrams in the ternary reciprocal salt system involving cyclohexylamine stearate (CS), cyclohexylamine palmitate (CP), 2,2'-dipyridylamine stearate (DS), and 2,2'-dipyridylamine palmitate (DP). The open circles represent metastable equilibria in the DS-DP system.

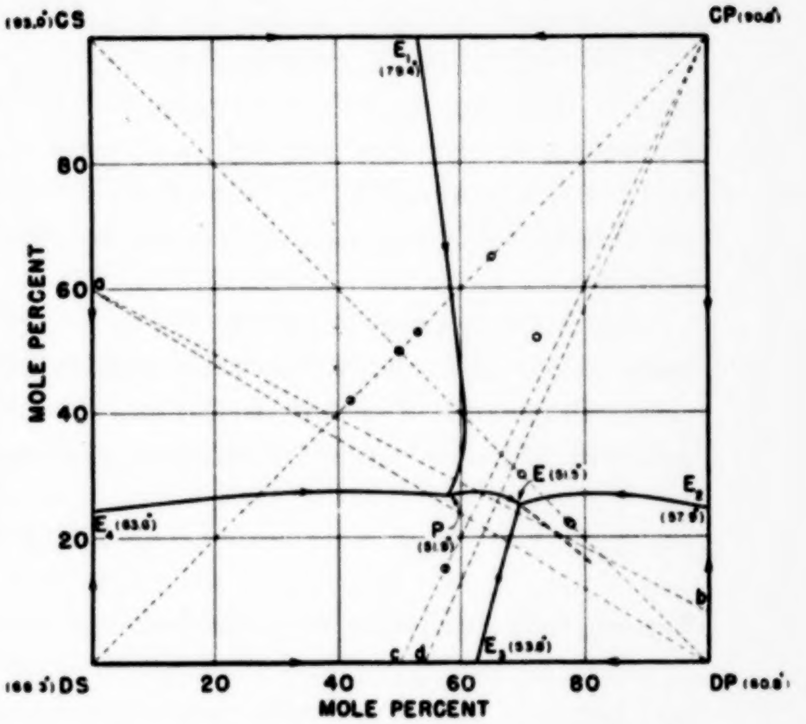

Fig. 2. Freezing point diagram for the ternary reciprocal salt system involving CS, CP, DS ,and DP. E_1, E_2, E_3, and E_4 are binary eutectics, P is the ternary peritectic, E is the ternary eutectic. The thin broken lines are projections of the quasi-binary systems investigated. Open circles are compositions for which heating curves were obtained.

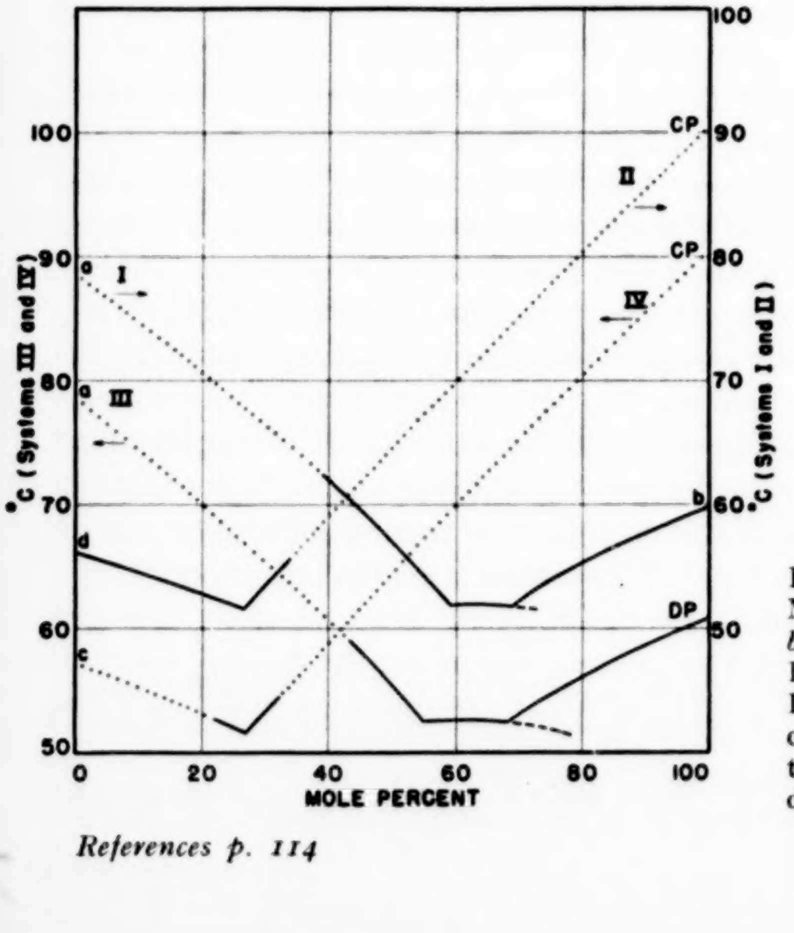

Fig. 3. Quasi-binary freezing point diagrams. Mixture *a* = 60% CS—40% DS; Mixture *b* = 92% DP—8% CP; Mixture *c* = 50% DS—50% DP; and Mixture *d* = 46% DS—54% DP. The dotted portions of the curves were obtained by interpolation from the isothermal projection of the ternary diagram.

for the DS-CP and CS-DP systems, on the other hand, would ordinarily be interpreted to indicate the formation of the 1:1 compounds DS:CP and CS:DP, respectively, the former melting congruently and the latter incongruently.

Actually, however, the equimolar mixture in the CS-DP system proved to be identical with that in the DS-CP system. They had the same primary freezing points, and, contrary to what would be predicted from the binary freezing point diagram, the equimolar DS-CP mixture did not freeze completely at the constant temperature, 63.1°C, but was found to contain perceptible liquid when equilibrated at 58.0°C. Furthermore, the freezing points of mixtures made by adding small amounts of CP or DS to an equimolar CS-DP mixture fell on the CP-DS diagram. Similarly, mixtures on the CS-DP diagram were made by adding CS or DP to an equimolar DS-CP mixture.

This freezing point behavior can be explained by the fact that the individual amine salts, when melted, probably dissociate into acid and amine molecules or the corresponding ions. They may therefore undergo double decomposition so that the following equilibrium exists in the liquid state:

$$\mathrm{CS} + \mathrm{DP} \rightleftarrows \mathrm{DS} + \mathrm{CP}$$

The system consisting of these four substances is a ternary system of the reciprocal or metathetical type. Though experimental data have been published for a number of inorganic reciprocal salt pairs, few, if any, organic salt systems have been investigated.

The graphical representation of the phase behavior of such systems has been developed by JÄNECKE[5]. Fig. 2 is a polythermal projection of the solid model formed by plotting primary freezing points vertically above a square base representing the various compositions in mole per cent. Each corner represents a pure substance, the sides represent binary compositions of substances with a common radical, and the interior includes all ternary compositions. Compositions made from a reciprocal pair fall on a diagonal.

The lines E_1P, E_2E, E_3E, E_4P, and EP represent all the univariant systems; *i.e.*, systems having two solids in equilibrium with the liquid. They correspond to the grooves formed by the intersections between the four bivariant surfaces of the solid model. Their position was defined by finding the temperature and composition of the apparent eutectic or peritectic points in a number of quasi-binary systems (Table I and Figs. 1 and 3), projections of which are shown in Fig. 2 as broken lines. The position of the eutectic grooves and the compositions and temperatures at the invariant ternary peritectic and eutectic points, P and E, respectively, were further established on the basis of the isotherms drawn through compositions having identical primary freezing points on each surface, as determined by interpolation in the various freezing point diagrams obtained from Table I. (These isotherms were also used to establish the data for the dotted lines in Fig. 3.) By extrapolation the ternary peritectic composition, P, was thus found to be 26.8 mole % CS, 15.2% DS, and 58.0% DP and its primary freezing point 51.9°C. The corresponding values for the ternary eutectic point, E, are 25.2% CS, 5.7% DS, and 69.1% DP for the composition and 51.5°C for the temperature.

It is apparent from Fig. 2 that the solid in equilibrium with the liquid along the

References p. 114

middle branch of the DS-CP diagram in Fig. 1 is crystalline CS. Similarly, CP is the solid phase in equilibrium on the corresponding portion of the CS-DP diagram and DS is the corresponding solid phase in the Mixture *a* - DP diagram in Fig. 3. Since the projection of the Mixture *a* - Mixture *b* system crosses the line PE, it is apparent from Fig. 2 that CP is the solid phase in equilibrium along the left end of the middle branch of the quasi-binary diagram for this system in Fig. 3 and DS is the solid in equilibrium along the right end of this branch.

METASTABLE EQUILIBRIA

The freezing point behavior of compositions near P and E in the DP and DS areas was complicated by the separation of one and, in some cases, two metastable phases which gave lower primary freezing points. The lowest-melting form was usually obtained when the sealed tubes containing these molten mixtures, preferably heated 10° to 20° above the melting point to destroy the crystal nuclei of the stable form, were cooled in air. They supercooled extensively and an increasing turbidity developed in the viscous liquid. Immediate immersion in a bath several degrees below the primary freezing point for the stable modification resulted in a rapid and complete clarification of the solution. After increasing lapses of time, however, immersion at this temperature resulted in a greater and greater residual turbidity which persisted until the primary freezing point of the stable modification was reached. Because of this gradual transformation, the solid-liquid equilibrium temperatures for this low-melting modification could not be determined.

The second type of metastable solid was evidenced by the freezing point behavior of two mixtures containing 54.60% and 73.76% DP, respectively, in the DS-DP system. These mixtures showed a reproducible, second primary freezing point, each about one degree below that for the stable modification (Table I and Fig. 1), resulting from metastable forms of DS and DP, respectively. This metastable form of DP may possibly be the same as that mentioned above.

The third type of metastable equilibrium, observed only in the DP area, is indicated by the data in Table I and the broken lines in Figs. 1 and 3. By referring to the projection of the quasi-binary system CS-DP in Fig. 2 it is apparent that the broken line in the freezing point diagram for this system in Fig. 1 represents equilibria between crystalline CP and liquid supersaturated with DP. Similarly, the broken lines for the two systems involving Mixture *a* in Fig. 3 represent equilibria between the stable crystalline modification of DS and liquid supersaturated with respect to DP. It can therefore be concluded that because of the tendency for the DP mixtures to supercool, the CP and DS crystallization surfaces extend into a metastable region below the DP surface of the three-dimensional model represented by Fig. 2. These metastable surfaces would be expected to intersect along an extension of PE as shown schematically by the broken line in Fig. 2.

HEATING CURVES

Cooling curves were not feasible because of the low rate of crystallization. However, heating curves were obtained for a number of mixtures, designated by the open circles in Fig. 2. The resulting curves depended in some cases upon the history and method of preparation of the sample. In general, they showed what appeared to be a eutectic halt, hereafter referred to as the halt, followed by a rather steep rise to within a few tenths of a degree of the surrounding shield temperature. Except for a few mixtures in the DS and DP areas there was no significant break at the primary freezing point of the stable modification though the sample always became clear and transparent within a few tenths of a degree of that temperature. The halt for similarly prepared samples, as measured by the break in the curve at the end of the halt, was usually reproducible to within about 0.3°C. For almost all mixtures the halt was at a slightly lower temperature than would be expected on the basis of the full lines in Fig. 2.

For all the designated mixtures in the CS and CP regions the halt came at 51.2 ± 0.2°C. Of these mixtures, that in the CS area to the left of the CS-DP diagonal was the only one for which there was a second break. This curve showed a rise in temperature after the halt, but less rapid than that of the surrounding shield, and then showed a break at about 52.4°C, slightly above the temperature for the ternary peritectic composition P.

From Fig. 2 it is apparent that the "stable pair" of reciprocal salts is CP and DS, since crystals of both are present at the invariant ternary peritectic and eutectic points. Considering the fact that this diagram is based on primary freezing point measurements obtained by the thermostatic method, the heating curves for the mixtures in the CP and CS areas can be considered in fair accord with what would be predicted from the diagram. The heating curves would indicate that the peritectic temperature is slightly higher and the eutectic temperature slightly lower than shown in Fig. 2. The fact that the major break in the heating curve is at the eutectic temperature in most of these samples can be explained by the absence of equilibrium conditions and the segregation of large crystals in the preparation of the solidified samples. Inhomogeneity was actually observed in the melting of a number of the samples.

The heating curve behavior of the mixtures in the DS and DP areas depended upon the method of preparation of the sample. Each of these samples, when prepared by heating well above the melting temperature and then allowing spontaneous crystallization, gave very similar heating curves. There was a rather indistinct halt in the vicinity of 48.0°C and then the temperature rose at a slightly higher rate than the surrounding shield, finally breaking toward the shield temperature at the primary freezing point predicted from Fig. 2. However, when these samples were remelted, seeded locally by touching the side of the sample tube with ice, and then allowed to crystallize, their heating curves were no longer similar. The samples in the DP area showed a distinct halt at about 50.5°C after which the temperature rose rapidly to that of the shield with no further break, though the melt did not become clear until the same primary freezing point had been attained. The mixture in the DS area when so prepared showed a halt at about 51.0°C but then the temperature rose at a slightly lower rate than that of the shield and finally showed a sharp break toward the shield temperature at the same primary freezing point as before.

The curves for ice-seeded samples were again in fair accord with Fig. 2, though the halt at 50.5°C for the mixtures in the DP area was 0.7° below the ternary eutectic temperature obtained consistently from the mixtures in the CP and CS areas. As mentioned below, however, this discrepancy could conceivably be attributed to the presence of a metastable eutectic composition.

The apparently anomalous heating curves for the spontaneously crystallized samples, showing a halt at about 48°C, led to the search for, and the discovery of, the various metastable equilibria in the compositions in the DS and DP areas. The freezing point data indicate that there is at least one metastable modification of both DS and DP, and, in addition that the stable forms of CP and DS can exist in metastable equilibrium with liquid supersaturated with respect to DP.

This implies, on the one hand, that in the solid model of which Fig. 2 is a projection there are other crystallization surfaces representing the equilibrium temperatures for the metastable forms of DS and DP, respectively. On the other hand, it is also implied that the crystallization surfaces for CP and for the stable form of DS can extend into a metastable region below the stable crystallization surface of DP and intersect along the extension of the projection PE. The point where the extension of PE reaches the metastable crystallization surface of DP would be a metastable ternary eutectic which could account for the halt at about 48°C observed in the seemingly abnormal heating curves for the mixtures in the DP and DS areas.

It will be apparent, however, that this is only one of the possible explanations for these curves. With the exception of the extension of PE, Fig. 2 shows the projections of the intersections of only the stable crystallization surfaces. If the metastable surfaces could be established there would be additional projections representing the following intersections: (1) the metastable DS surface with the stable DP surface, (2) the stable DS surface with the metastable DP surface, (3) the metastable DS surface with the metastable DP surface, (4) the (stable) CP surface with the metastable DP surface, and possibly the (stable) CP surface with the metastable DS surface. Correspondingly, a number of possible metastable ternary eutectic points could also be visualized. Considerably more information will obviously be necessary to explain completely all the possible aspects of the freezing point behavior of the system.

ACKNOWLEDGEMENT

The authors are indebted to LAWRENCE E. BROWN for the nitrogen analyses.

SUMMARY

Binary and quasi-binary freezing point data have been obtained to establish the freezing point diagram for the ternary reciprocal salt pair system involving cyclohexylamine stearate, cyclohexylamine palmitate, 2,2′-dipyridylamine stearate, and 2,2′-dipyridylamine palmitate. The compositions and primary freezing points of the ternary peritectic and eutectic mixtures have been determined. Apparent anomalies in the heating curves for selected compositions have been explained on the basis of the existence of metastable equilibria.

RÉSUMÉ

Les auteurs ont déterminé des données de point de congélation binaire et quasi-binaire afin d'établir le diagramme de point de congélation du système ternaire de paires de sels réciproques contenant les stéarate et palmitate de cyclohexylamine, et les stéarate et palmitate de 2.2′-dipyridylamine. Les compositions et les points de congélation primaires des mélanges ternaires péritectique et eutectique ont été déterminés. Des anomalies apparentes dans les courbes de chauffage de certaines compositions choisies ont été expliquées en se basant sur l'existence d'équilibres métastables.

ZUSAMMENFASSUNG

Binäre und quasi-binäre Gefrierpunkte wurden bestimmt um das Gefrierpunktsdiagramm des folgenden Systemes reziproker Salzpaare aufzustellen: Cyclohexylaminstearat und -palmitat,

2.2′-Dipyridylaminstearat und -palmitat. Die Zusammensetzungen und primären Gefrierpunkte der ternären peritektischen und eutektischen Gemische wurden bestimmt. Scheinbare Anomalien der Erhitzungskurven von ausgesuchten Zusammensetzungen wurden auf Grund von metastabilen Gleichgewichten erklärt.

REFERENCES

[1] E. L. Skau, *J. Phys. Chem.*, 33 (1929) 951-954; E. L. Skau and W. Bergmann, *J. Org. Chem.*, 3 (1938) 166-174; E. L. Skau and H. Wakeham, *Melting and Freezing Temperatures* in Weissberger, *Physical Methods of Organic Chemistry*, 2nd ed., Interscience, New York, N.Y., 1949, Vol. I, Part I, pp. 99-100.

[2] E. L. Skau, F. C. Magne and R. R. Mod, unpublished.

[3] F. C. Magne and E. L. Skau, *J. Am. Chem. Soc.*, 74 (1952) 2628-2630.

[4] E. L. Skau, *Proc. Am. Acad. Arts Sci.*, 67 (1932) 551-576; *J. Phys. Chem.*, 37 (1933) 609-614.

[5] E. Jänecke, *Z. physik. Chem.*, 64 (1908) 305-327.

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EXPERIMENTAL METHODS FOR THE DETERMINATION OF PURITY BY CRYOSCOPY IN CURRENT USE AT THE CHEMICAL RESEARCH LABORATORY, TEDDINGTON

by

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For the determination of purity of organic substances three methods will be described:

1. A freezing-point procedure for use with hygroscopic and non-hygroscopic material in estimating absolute purity.
2. A melting-point procedure for absolute purity estimation based on a new method of treating the data.
3. A method for the inter-comparison of purity of several samples, suitable for routine control of high-purity materials in a plant process.

1. FREEZING-POINT PROCEDURE

An essential condition for the application of the freezing-point method for estimating absolute purity is the maintenance of thermodynamic equilibrium between the liquid and crystallized solid while heat is withdrawn from the system at a controlled rate. In many examples of apparatus devised for this purpose, equilibrium conditions are achieved by the use of motor-driven stirrers, both of the rotating and reciprocating types[1,2,3,4,5,6,7]. The liquid may be protected from contact with atmospheric moisture by the passage over the liquid surface of a stream of dry, filtered air which can escape through the stirrer gland. An alternative method for securing good mixing and preventing ingress of air has been used by STULL[8], who employed a sealed-in stirrer operated by a solenoid, but care must be taken to avoid electrical interference with the temperature measuring device.

With all types of mechanical agitation, the stirrer ceases to operate when only a fraction of liquid is frozen, and thereafter the rate of cooling is changed and results in a change in direction of the freezing curve at the point where the stirrer stops. SCHWAB AND WICHERS[9] have circumvented this difficulty by passing a stream of gas bubbles through the liquid by means of a sintered glass diaphragm, but where a number of compounds are to be examined, the cleaning of the diaphragm can be laborious and time-consuming.

When the measurement of temperature during the freezing is made by a platinum resistance thermometer, a sufficient quantity of material is necessary to secure the requisite conditions of immersion of the sensitive element. The employment of 100 ml is frequently required, and in many cases this may consist of the whole of the available material, so that a procedure carried out with a much smaller sample is advantageous, particularly when the comparative method of adding successive amounts of impurity, as recommended by SCHWAB AND WICHERS, is adopted.

In the apparatus and procedure now utilised in the Chemical Research Laboratory, attempts have been made to surmount some of the foregoing difficulties. Adequate mixing has been obtained by applying a pulsating pressure of dry gas to the liquid surface in such a way as to produce oscillations in a sealed U-shaped column of the sample being frozen.

By this means the mixing of the liquid phase continues until practically all of the sample has been frozen, while at the same time moist air is excluded from the material. The apparatus is easily cleaned and assembled, and only 10-20 ml of liquid are required for each determination. Thermo-couples with the reference junction maintained at the triple-point of water are used for measurement of temperature.

The apparatus in current use is substantially the same as that already described[10], and differs only in the following details: The length of the U-tube arms have been increased from 38 to 48 cm to give greater immersion in the surrounding Dewar vessel, and thus minimise the heat transfer between the sample and the atmosphere. The stainless steel helices situated in each arm of the U-tube have now been replaced by silver coils of the same dimensions, thereby securing advantages of better heat conductivity and resistance to chemical attack. Originally temperature measurements were made using thermistors (thermally sensitive resistance elements) but copper-constantan thermo-couples are now employed. From long-term observations it was established that the absolute electrical resistance of thermistors changed slightly, rendering frequent calibrations necessary. Moreover, it was found that in the temperature region of —130 to — 150°Celsius, the resistance of a 200 ohms thermistor rose to several megohms, so that the operation of the Wheatstone bridge in which it was incorporated became difficult and the recorder measuring the out-of-balance current from the bridge was slow in response to temperature changes. With the copper-constantan thermo-couple now used the measuring junction is situated at the bottom of the glass pocket which extends inside one arm of the U-tube to within 2 mm of the bottom, since visual inspection has shown that the last drops of liquid collect at this point at a time when the whole sample is nearly frozen. The reference junction of the thermo-couple is maintained at the triple-point of water, *i.e.* + 0.01° Celsius in a cell constructed and prepared by the methods described by BARBER, HANDLEY AND HERINGTON[11]. Heavy single-core copper leads of 17 SWG are used as connections between the junctions of the thermo-couple and the measuring potentiometer, which is a 4-dial vernier instrument permitting observations to 0.1 microvolt. The potentiometer is housed in a temperature-controlled room adjacent to the freezing-point apparatus and during the course of freezing readings are taken at intervals of two minutes.

To induce crystallization when the sample has been cooled to its freezing point under carefully controlled conditions, *i.e.*, when a constant cooling rate of approximately 0.2°Celsius per minute has been attained, two methods are used. In one case, a stainless steel ball-bearing $\frac{3}{32}$ in. diameter, held in a glass pocket attached to the apparatus, is cooled below the freezing point of the specimen and dropped by manipulation of an external magnet into the pulsing liquid, or alternatively, a small

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crystal of the solidified specimen is projected into the liquid. While the latter method involves opening a port of the apparatus and temporary stoppage of the mixing of the liquid, no moisture can enter the apparatus since the dry gas which normally produces the pulses escapes this way when the cap is removed.

From the time-temperature relationship recorded, the freezing curve is plotted and the whole procedure is repeated, under identical conditions, several times if desired, after adding known amounts of impurity. The resulting series of curves are of the type as shown by HERINGTON[12], who also describes the simple treatment of the data to obtain the purity of the original compound.

Table I lists compounds whose purity has been successfully estimated in the apparatus with the methods described.

TABLE I

COMPOUNDS WHOSE PURITY HAS BEEN DETERMINED IN THE C.R.L. FREEZING-POINT APPARATUS

- *Aromatic compounds*
  - Benzene
  - Toluene
  - *o*-Xylene
  - *m*-Xylene
  - *p*-Xylene
  - Naphthalene
  - 2-Methylnaphthalene
  - Benzoic acid
- *Paraffins*
  - *n*-Butane
  - *n*-Pentane
  - *n*-Octane
  - *n*-Heptane
  - *n*-Decane
- *Naphthenes*
  - Cyclopentane
  - Methylcyclopentane
  - Cyclohexane
- *Olefines*
  - *iso*-Butene
  - *cis*-2-Butene
  - Cyclopentene
- *Heterocyclic bases*
  - Pyridine
  - α-Picoline
  - β-Picoline
  - γ-Picoline
  - 2,5-Lutidine
  - 2,6-Lutidine
  - Piperidine
  - Quinoline
  - *iso*-Quinoline
- *Phenols*
  - Phenol
  - *o*-Cresol
  - *p*-Cresol
  - 2,6-Xylen-1-ol

2. MELTING-POINT PROCEDURE

In the estimation of purity by the cryoscopic method substances may be encountered which exhibit a high viscosity near the freezing-point; other materials form crystals which grow in a solid mass and not as a dispersal of crystals throughout the liquid. Either of these conditions makes it difficult to attain temperature equilibrium. There remains a third class of compounds which fails to crystallise at its freezing-point using any of the available methods to induce crystallisation. It follows that the freezing-point method cannot be used for any of these compounds, but the alternative of measuring purity from a melting point curve may be applicable.

For this purpose we have developed at the Chemical Research Laboratory a simple melting-point apparatus which is designed to give efficient heat transfer throughout the test sample during the melting (Fig. 1). The sample is contained in a cylindrical cell constructed in silver since this metal satisfies the conditions of low specific heat, good thermal conductivity and high resistance to chemical attack. Types of

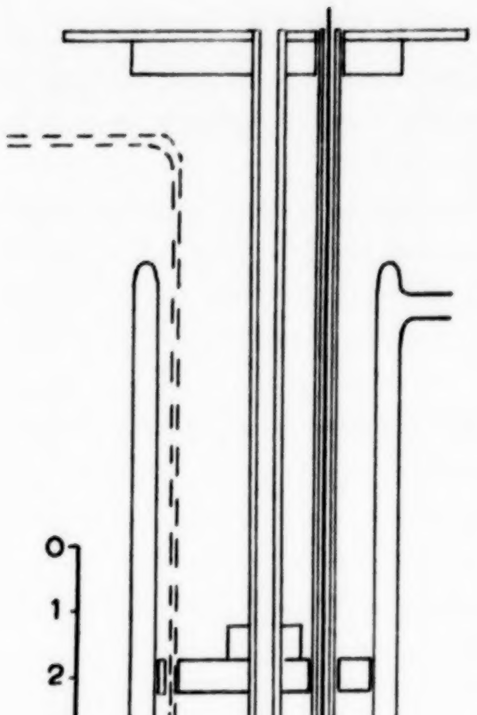

Fig. 1. Melting-point apparatus.

materials examined in this silver cell, without evidence of corrosion, include hydrocarbons, pyridine bases and phenols. The cell is equipped with two ports which can be closed by silver screwed plugs compressing thin lead washers, and to assist internal heat transfer a number of thin horizontal silver vanes 0.005 in. thick are arranged in the interior of the cells at 2 mm distance. They surround the central thermo-couple pocket and extend to the inner walls, so that no part of the material is farther than 1 mm from a metal conductor. To facilitate the filling of the cell, a narrow tube extends from one port almost to the bottom of the cell, and a series of holes drilled in line in the silver vanes, diametrically opposite to the filling tube, assists in removal of air. The cell is positioned inside two concentric copper shields, the outer one of which is wrapped along its length with an electric resistance heater. The complete assembly is supported by means of a hollow Bakelite tube, inside a cylindrical Dewar vessel at the average depth of 15 in. The leads of a copper-constantan thermo-couple pass from the pocket in the cell to the exterior through a second hollow Bakelite tube which is off-set from the central supporting tube. For convenience of assembling the apparatus, provision is made for the outer radiation shield to slide along the Bakelite tubes and closure of inner and outer compartments of the chambers is made with close fitting circular copper plates. As in freezing-point experiments, the thermo-couple reference junction is maintained at the triple-point of water, and readings are taken on a 4-dial vernier potentiometer.

The sample is charged in its molten state into the cell and for materials whose melting point is above room temperature, this operation is carried out in a glass-fronted heated cabinet. The cell is then closed, mounted inside the radiation shield unit with thermo-couple in position and lowered inside the Dewar vessel. Thermo-couple and electrical connections are made, and the cell is then rapidly cooled by projecting a stream of liquid nitrogen down the hollow supporting tube on to the top of the silver cell. The freezing of the sample is observed by taking potentiometer readings, since a perceptible halt is shown in the temperature fall when freezing takes place. Cooling by means of the refrigerant is continued to a point at least 20°Celsius below the freezing point.

After a period of approximately one hour, in which the system is allowed to attain thermal equilibrium, a heating current is passed through the resistance winding on the outer radiation shield so that a steady temperature rise of 0.2°Celsius per minute

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is achieved when the sample is approximately 10° below its melting point. Temperature readings are taken at 2 minute intervals and continued until all the sample is melted. Repeat experiments are then carried out after adding known amounts of impurity in sequence, and by plotting temperatures versus time, a series of melting curves, as shown in Fig. 2, is obtained. These curves were obtained with 99.995 moles % benzene and with this material when two additions of impurity had been made.

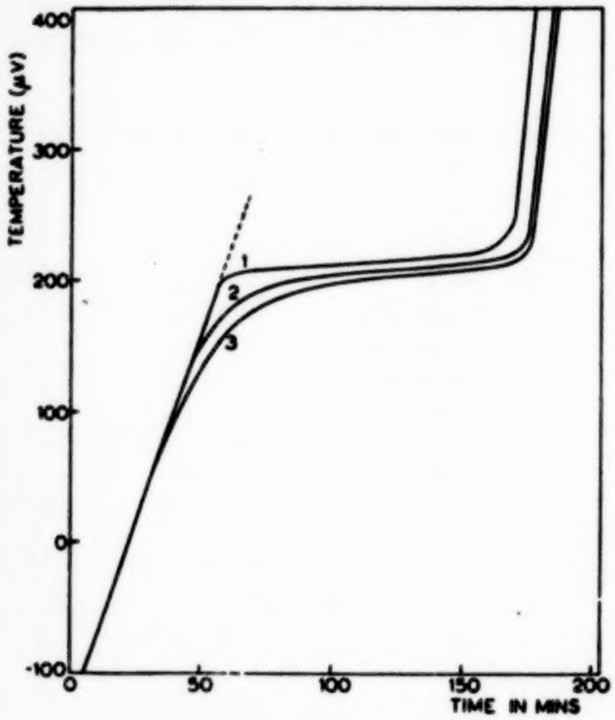

Fig. 2. Melting-point curves.
Curve 1: 99.995 moles % benzene
Curve 2: 99.94 moles % benzene
Curve 3: 99.885 moles % benzene

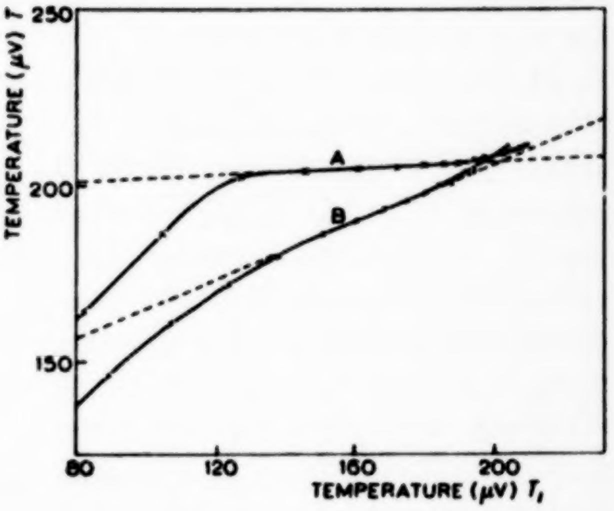

Fig. 3. Temperature *vs.* temperature plot of melting curves.
A: curve 1 plotted against curve 2 (Fig. 2)
B: curve 2 plotted against curve 3 (Fig. 2)

TABLE II

EXAMPLES OF DETERMINATION OF PURITY BY THE MELTING-POINT PROCEDURE

Melting curves examined	*Impurity present in original material moles %*	*Added impurity moles %*	*Calculated impurity moles %*
1 and 2	0.005 ± 0.002	0.0	0.002
2 and 3	0.005 ± 0.002	0.055	0.065
3 and 4 (latter not shown)	0.005 ± 0.002	0.11	0.12
4 and 5 (not shown)	0.005 ± 0.002	0.23	0.28

If the commencement of deviation from the straight-line plot of approach warming be taken as the initial melting point, then in the manner described by Herington[12], by plotting the temperature of one melting sample against the temperature of another at equal time intervals after the initial melting point, a straight line is obtained of which the slope represents $x/(x+x_1)$, where x is the impurity present in the sample originally, and x_1 is the known amount of added impurity; hence x can be readily determined.

Fig. 3 was derived from the data presented in Fig. 2 and as can be seen straight lines are obtained from which the amount of original impurity can be calculated.

Experimental results obtained from this series of three melting curves with benzene, whose purity had independently been determined by the freezing method, are given in Table 2. Also included are calculations obtained after making a third and fourth addition of impurity.

TABLE III

COMPOUNDS WHOSE PURITY HAS BEEN DETERMINED IN THE MELTING-POINT APPARATUS DESCRIBED ABOVE

Hydrocarbons
- *iso*-Propyl-benzene
- *iso*-Pentane
- *iso*-Octane
- Methylcyclopentane

Pyridine bases
- β-Picoline
- 2,4-Lutidine
- 3,5-Lutidine

Phenols
- *m*-Cresol
- 2,3-Xylen-1-ol
- 2,4-Xylen-1-ol
- 2,5-Xylen-1-ol
- 3,5-Xylen-1-ol
- 3,4-Xylen-1-ol
- *o*-Ethylphenol

3. DIFFERENTIAL PROCEDURE

The preparation of organic chemicals in modern plant processes is frequently controlled by specifications which require a high standard of purity, and these specifications often stipulate the maximum amount of impurity, in terms of moles per cent, that may be present. The intricate apparatus and precise techniques required for the determination of purity by freezing-point or melting-point determinations render these methods difficult, and moreover the time involved in these procedures can result in delays, particularly where rapid adjustments to the process are necessary. As a means of providing a practical analytical tool in these circumstances, an apparatus has been devised at Teddington, which enables a simultaneous comparison of the purity of five samples to be made, by plotting the differential melting-point curves of each sample under identical conditions. The apparatus can be operated under routine procedure and with the employment of automatic recording for the curves, results can be obtained in 4 hours.

The principal components of the apparatus (Fig. 4) consist of five small silver cells and a solid copper cylindrical block which is bored with six wells in symmetrical pattern to accommodate the cells. The cells are constructed of metal tube 0.02 in. wall thickness and are $\frac{5}{8}$ in. diameter, $1\frac{3}{4}$ in. long with a capacity of 6.0 to 6.5 ml. A central thermo-couple pocket of silver tube $\frac{3}{32}$ in. internal diameter extends from the bottom of the cell to a distance of $1\frac{3}{8}$ in. The filling and emptying is carried out through a single port at the top, which can be sealed with a screwed silver plug and thin lead washer. Attainment of good thermal conductivity inside the cell is achieved by a packing of silver wire gauze, which is arranged in a symmetrical pattern by folding in narrow loops between the central pocket and the cell walls (Fig. 4a). The copper block $3\frac{1}{8}$ in. diameter and $3\frac{1}{2}$ in. long has six wells $\frac{3}{4}$ in. diameter bored symmetrically around the centre to a depth of $2\frac{1}{8}$ in., and it is wrapped along its length with a spiral resistance heater. In five of the cavities the silver cells are supported so that they are equidistant from the walls of the copper-block, and are thermally insulated at the base by means of asbestos spacing pieces. The sixth well contains a solid copper cylinder of the same dimensions as the calorimeter cells, and bored with six holes $\frac{3}{64}$ in. diameter to a depth of $1\frac{3}{8}$ in. By means of a hollow Bakelite rod, $\frac{1}{2}$ in. external diameter, $\frac{1}{4}$ in. internal diameter, the copper block and cells are supported inside a close-fitting glass sheath, which in turn is surrounded by a Dewar vessel. The recessing of the base of the copper block to a depth of $\frac{1}{2}$ in. provides a means whereby a thermo-couple junction can be inserted upwards into the central pocket of each cell through a hole bored between the base of the block and each cavity. The junction of each thermo-couple is protected by a thin stainless steel sheath which is cemented in position and acts as a guide when the cells are placed inside the wells. The second junction of each thermo-couple is inserted in a hole in the small copper cylinder, so that a differential temperature is recorded between the five silver cells and this copper cylinder. By means of a sixth thermo-couple junction, also inserted in the small copper cylinder but with its reference junction in an ice-bath, the temperature changes of the system *i.e.* the warming rate, can be measured. All the thermo-couple leads are conducted through the hollow Bakelite supporting rod to the adjacent measuring and recording equipment. The bottom of the copper block is sealed with a circular plate $\frac{1}{4}$ in. thick, while a massive lid $\frac{1}{2}$ in. thick slides down the Bakelite tube to form an upper seal by means of a tapered joint.

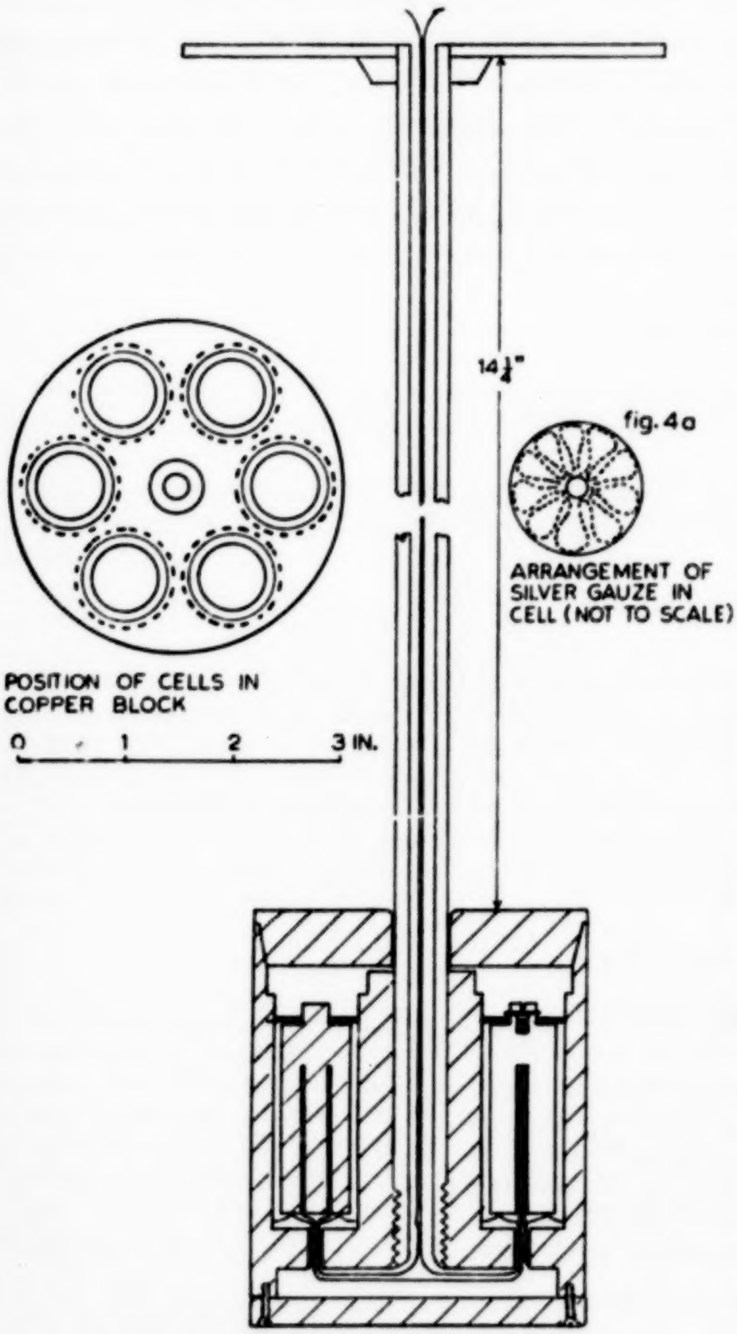
14¼"
fig. 4a
ARRANGEMENT OF SILVER GAUZE IN CELL (NOT TO SCALE)
POSITION OF CELLS IN COPPER BLOCK
0
1
2
3 IN.

Fig. 4. Multi-cell differential thermal analysis apparatus.

The following procedure, with benzene as example, is representative of the operations carried out in the apparatus: The five cells are cleaned with solvent, dried and weighed empty. They are then charged with a uniform weight of each sample by transfer from a pipette. After sealing with the screwed plug, they are re-weighed, placed in the cavities inside the copper block and the copper lid lowered in place. The copper block is then suspended inside a closely fitting glass sheath to a mean depth of 15 inches, and connections are made from each differential thermo-couple to a multi-point, 10 mV recorder. The thermo-couple for measuring the actual temperature of the small copper cell is connected to a dial potentiometer, and electrical connections are made so that current may be fed to the block heater from a variable voltage output transformer.

The copper block inside its glass sheath is now immersed in a cooling bath and cooled at a very fast rate, *e.g.* 2°-3°/min until the five samples are approximately 30° below their freezing point, when the cooling bath is removed and replaced by a close-fitting cylindrical Dewar vessel. An interval of approximately 20 minutes is then allowed to remove thermal gradients inside the system and also, in cases where crystal growth is slow, to complete the freezing. The freezing of the samples can be observed on the recorder chart since it is denoted by a rapid change in direction of the plot across the chart of the recorded differential temperature of each sample. When freezing is complete, the plot rapidly reverts to the original position on the chart and continues in a straight line.

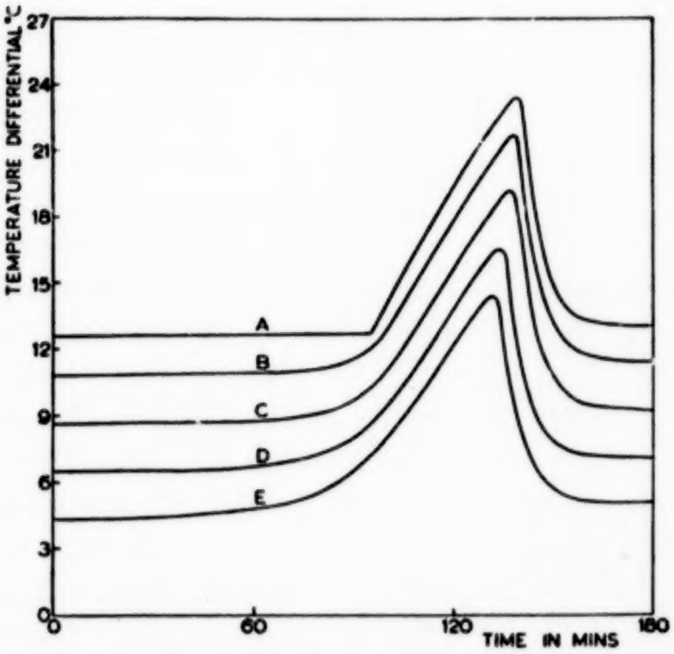

Fig. 5. Differential melting point curves.
A: 99.99 moles % benzene
B: 99.92 moles % benzene
C: 99.84 moles % benzene
D: 99.67 moles % benzene
E: 99.35 moles % benzene

At the end of the interval, heat is applied by means of the resistance heater wrapped round the copper block and, from observations on the measuring potentiometer, adjustments are made to the heating current to obtain a steady warming rate in the region of 0.2° to 0.25°Celsius per minute. It is essential that a constant warming rate be attained at a stage when the specimens under test are at least 10° below their melting point. Thenceforward the operation of the apparatus is automatic and the plot of each differential thermo-couple on the recorder chart continues in a straight line until melting begins, at which point a deviation is shown on the plot. This deviation, representing a differential temperature between the specimen and the small copper cylinder, continues to a maximum until all the sample is melted, when the cell and contents hasten to regain temperature equilibrium with the surrounding copper block and the recorder plot rapidly returns to its original position in the chart. At the conclusion of the experiment the cells are re-weighed to establish that no leakage has occurred.

An example of the curves obtained from five samples of benzene of differing purity, ranging from 99.995 to 99.35 moles % is shown in Fig. 5. These curves show the general features discussed by HERINGTON[12], Thus the least pure specimen gives a curve which is first to deviate from the straight line plot and moreover, by examining the point of deviation it is easy to distinguish between samples of 99.995 and 99.92 moles % purity. Further, the purer the sample the later does the peak appear and the greater is the height of the peak.

ACKNOWLEDGEMENTS

I wish to thank Mr. D. HARROP who has rendered valuable assistance by carrying out numerous experiments in the estimation of purity of compounds by freezing-point and melting-point techniques.

The work described above has been carried out as part of the research programme of the Chemical Research Laboratory, and this paper is published by permission of the Director of the Laboratory.

SUMMARY

A description is given of apparatus devised to evaluate purity by freezing-point and melting-point procedures. Both methods yield regular curves from which data can be obtained in the manner described to determine the purity after simple treatment. Examples of experimental melting curves and results are given.

As a means of providing process control in the production of high-purity chemical compounds, an apparatus has been developed which simultaneously makes a comparison of purity between several samples, one of which is a reference specimen of known purity, by plotting their differential melting-point curves.

RÉSUMÉ

L'auteur décrit des appareils construits pour évaluer la pureté par des procédés de point de congélation et de point de fusion. Les deux méthodes donnent des courbes régulières à partir desquelles l'on peut obtenir des données de la manière décrite pour la détermination de la pureté après traitement simple. Des exemples de courbes et de résultats expérimentaux sont donnés.

Afin d'obtenir un procédé de contrôle pour la production de composés chimiques de grande pureté, un appareil a été développé qui compare simultanément la pureté de plusieurs échantillons dont l'un est un spécimène de référence de pureté connue, en dessinant leurs courbes de fusion différentielles.

ZUSAMMENFASSUNG

Der Verfasser beschreibt Apparate die entworfen wurden um den Reinheitsgrad mit Hilfe von Gefrier- und Schmelzpunktverfahren zu ermitteln. Beide Methoden ergeben regelmässige Kurven aus denen man Angaben in der Weise entnehmen kann, wie sie zur Bestimmung des Reinheitsgrades nach einfacher Behandlung beschrieben wurde. Beispiele von experimentellen Kurven und Resultaten werden angeführt.

Als Hilfsmittel bei der Kontrolle der Produktion chemischer Verbindungen von hohem Rein, heitsgrad wurde ein Apparat entwickelt der gleichzeitig die Reinheit mehrerer Proben vergleichtderen eine Vergleichssubstanz von bekannter Reinheit ist, und zwar durch Aufzeichnung ihrer Differential-Schmelzpunkts-Kurven.

REFERENCES

[1] W. P. White, *J. Phys. Chem.*, 24 (1920) 393.
[2] S. Kaye, *Anal. Chem.*, 24 (1952) 1038.
[3] W. Crawford and C. L. A. Harbourn, *Anal. Chem.*, 27 (1955) 1449.
[4] B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, 26 (1941) 591.
[5] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, 35 (1945) 355.
[6] A. R. Glasgow, N. C. Krouskop, Joan Beadle, Gladys D. Axilrod and F. D. Rossini, *Ind. Eng. Chem., Anal. Ed.*, 20 (1948) 410.
[7] A. R. Glasgow, N. C. Krouskop and F. D. Rossini, *Anal. Chem.*, 22 (1950) 1521.
[8] D. R. Stull, *Ind. Eng. Chem., Anal. Ed.*, 18 (1946) 234.
[9] F. W. Schwab and E. Wichers, *Temperature - Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, (1941), p. 256.
[10] E. F. G. Herington and R. Handley, *J. Chem. Soc.*, (1950) 199.
[11] C. R. Barber, R. Handley and E. F. G. Herington, *Brit. J. Appl. Phys.*, 5 (1954) 41.
[12] E. F. G. Herington, *Anal. Chim. Acta.*, 16 (1957) 15.

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THE EVALUATION OF CRYOSCOPIC CONSTANTS FOR USE IN THE DETERMINATION OF PURITY BY THE FREEZING POINT METHOD

by

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INTRODUCTION

The estimation of purity by the cryoscopic method has been developed by ROSSINI and co-workers[1,2,3] and has now been adopted by the ASTM as a Standard Method of Test[4].

The basic equation used in this work is:

$$\text{Mole per cent impurity} = A(T_{fo} - T) \qquad (1)$$

where $A = \dfrac{100 \triangle H_{fo}}{R T_{fo}^2}$ = cryoscopic constant, mole per cent /°C, where

$\triangle H_{fo}$ = heat of fusion

R = gas constant

T_{fo} = absolute freezing point of major component when 100 per cent pure

T = absolute temperature of equilibrium

Procedures in use for the evaluation of the cryoscopic constant, which is necessary for use in the calculation of purity by this method are (1) the determination of the heat of fusion calorimetrically and substitution of this value in the equation relating the heat of fusion and cryoscopic constant, (2) direct determination of the cryoscopic constant by measurement of the lowering of the freezing point due to the addition of a small amount of impurity; and (3) estimation of the heat of fusion by comparison of the freezing or melting curve of the material with that of a compound of similar structure, of which the heat of fusion is known, and which freezes within ± 20°C of the given compound.

The disadvantages of these methods are that the first method requires special equipment, contamination of the sample will result if the lowering of freezing point is measured as in the second method, and in method 3 the comparison may not be possible.

This present work suggests a way in which the standard equipment for the determination of the freezing or melting point may be converted into a simple calorimeter, wherein the heat of fusion may be measured, and hence the purity calculated. It is not suggested that the method outlined in this paper should replace any of the existing procedures in use for the accurate determination of the heat of fusion, but it should prove useful in laboratories where the routine determination of purity of a range of compounds rather than the precise measurement of the heat of fusion or the cryoscopic constant is the prime concern.

MATERIALS EMPLOYED

The materials used are listed in Tables I and II, together with their purities determined by the freezing point method.

The hydrocarbons used were either prepared or purified at the BP research laboratories, and form part of the stock of pure materials.

Details of the preparation and purification of 3-methyl-2-thiabutane, 4-thiaheptane, thiacyclopentane and thiacyclohexane have been published[5,6].

The thiophene was also prepared in these laboratories, and the ethyl alcohol and ethyl acetate were commercial materials.

EXPERIMENTAL

(a) Apparatus

The freezing point apparatus in use in these laboratories follows closely that first described by GLASGOW, STREIFF AND ROSSINI[1].

In this method, the material under examination is frozen and melted in a double-walled tube, the rate of heat transfer from the refrigerant or heating bath to the sample or vice versa, being controlled by the vacuum between the walls of the tube, which may be varied. Modifications were made to the equipment in that a rotating stirrer is now used, and that an aluminium tube may be inserted to reduce the volume when dealing with small quantities of material[7].

For the determination of heats of fusion, the rotary stirrer was replaced by a system of aluminium vanes, which assisted in the even distribution of heat throughout the sample. Each vane was made from 0.75 mm sheet, was 25.5 mm in diameter, and 60 mm long. Four vanes were fitted together at the bottom by a series of slots, and held rigid by aluminium wire wound through the vanes in a spiral. A central section, 7.5 mm diameter, was cut from each vane to permit entrance of the thermometer. The assembly, which is shown in Fig. 1, was shaped to fit closely between the walls of the freezing tube.

A diagram of the complete apparatus is given in Fig. 2.

Temperatures were measured by a platinum resistance thermometer, the resistance being measured by a Mueller Bridge (Leeds and Northrup Company) as recommended by the ASTM[4].

(b) Procedure

The sample (25 ml) was weighed into the freezing tube containing the vane assembly, and the thermometer inserted into the central well.

Cooling of the tube and sample was effected with the usual refrigerants, *viz.* liquid nitrogen or solid carbon dioxide/acetone mixtures. Ice or hot water (thermostated to ± 1°C) were used for the heating baths. The freezing tube was immersed to the same depth in all experiments. The difference in temperature between the freezing

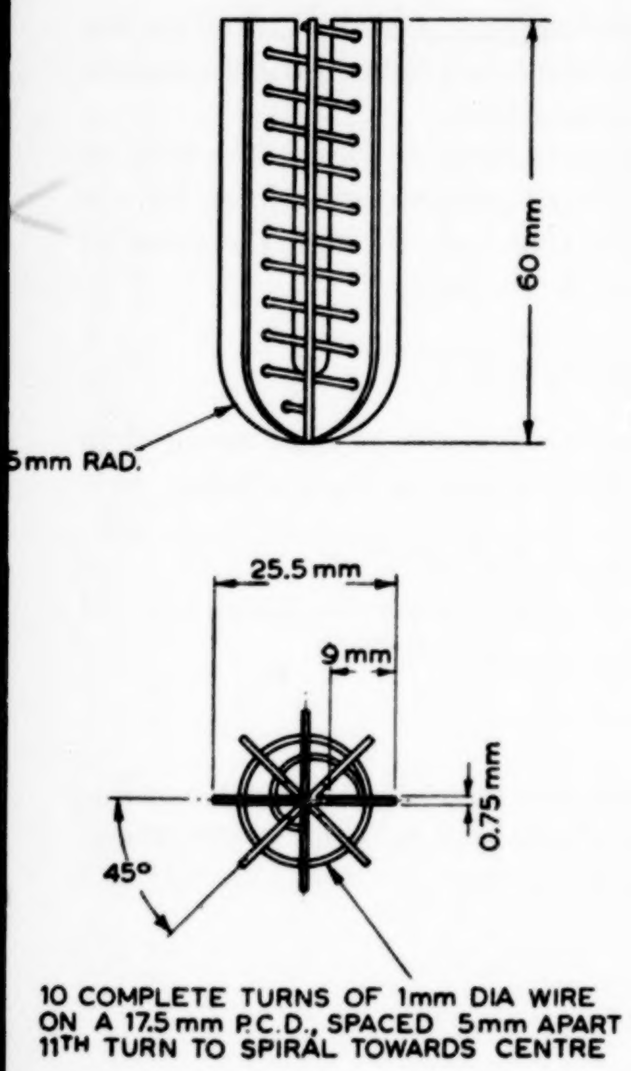
5mm RAD.
60 mm
25.5 mm
9 mm
0.75 mm
45°
10 COMPLETE TURNS OF 1mm DIA WIRE
ON A 17.5mm P.C.D., SPACED 5mm APART
11TH TURN TO SPIRAL TOWARDS CENTRE

Fig. 1. Heat of fusion apparatus. Calorimeter vanes.

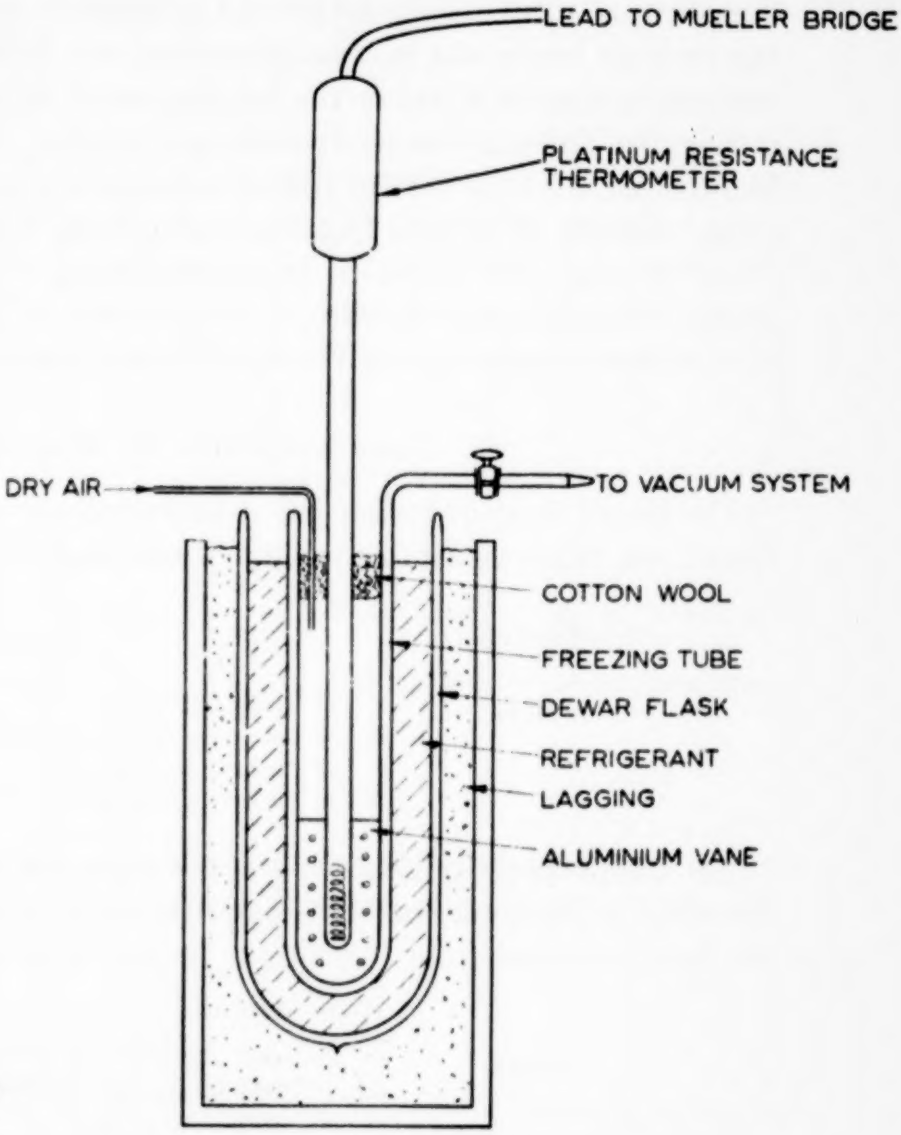
LEAD TO MUELLER BRIDGE
PLATINUM RESISTANCE THERMOMETER
DRY AIR
TO VACUUM SYSTEM
COTTON WOOL
FREEZING TUBE
DEWAR FLASK
REFRIGERANT
LAGGING
ALUMINIUM VANE

Fig. 2. Apparatus for the determination of cryoscopic constant.

point of the material and the heating or cooling liquids was kept to at least 50°C in order to minimise the variation of rate of heat transfer between the bath and the sample due to variations in the temperature head.

The sample was cooled rapidly to about 30°C above the freezing point, at which time the space between the walls of the tube was evacuated. By adjustment of the vacuum it was possible to vary the cooling rate according to the heat of fusion of the sample (an indication as to whether the heat of fusion of unknown compounds is high or low is obtained by examination of the curves obtained when determining the freezing or melting point). For materials having a low heat of fusion, a low cooling rate was required so that the time of freeze could be measured accurately, and for those with a high value a fast cooling rate was used to speed up the determination, *e.g.* for *n*-octadecane, $H_{fo} = 14.815$ Kcal/mole, the rate of change of temperature was 2.67°C/min, giving a time of freeze of 25 min. For cyclohexane, $H_{fo} = 0.6398$ Kcal/-mole, the time of freeze was 20.2 min at a rate of 0.56°C/min.

Readings of the resistance of the thermometer were taken at intervals of one minute with the Mueller Bridge to an accuracy of 0.001 ohms (corresponding to 0.01°C) during the cooling and freezing of the sample, until the rate of change of temperature after the material had completely frozen was constant. In the case of the melting curve the reverse procedure was followed. When the temperature had reached at least 30°C below the freezing point, a heating bath was substituted for the refrigerant, the vacuum readjusted, and readings of resistance taken until the sample had melted, and the rate of rise of temperature was constant.

An example of typical freezing and melting curves is given in Fig. 3. The time of freeze or melt was obtained by extrapolating the time-temperature curves for the liquid and solid, and drawing a line parallel to the time axis through the point of maximum temperature on the equilibrium portion of the curve.

CALCULATION OF HEAT OF FUSION

The latent heat of fusion per mole is defined as the quantity of heat required to freeze one gram molecular weight of material with no change of temperature.

Therefore $$\Delta H_{fo} = \frac{M\,Z\,K}{g} \text{ cal/mol} \qquad (2)$$

where
Z = time of freeze
K = net rate of heat transfer cal/min
g = weight of material
M = molecular weight

For the purposes of this work, it was assumed that the rate of heat transfer during the time of freeze or melt was equal to that just above the freezing point, hence, the heat removed from the sample in one minute is

$$K = \Delta t c g \text{ cal} \qquad (3)$$

where
c = heat capacity of sample cal/g/°C
Δt = rate of change of temperature °C/min
g = weight of liquid

The total heat removed from the apparatus in one minute is

$$K + (\Delta t c_1 g_1) \qquad (4)$$

where c_1g_1 is a constant at any temperature which depends on the heat capacity of the apparatus, and the heat loss from the apparatus.

To calculate the heat of fusion from equation (2) it is necessary to know the heat capacity of the material at its freezing point. Although figures were available for all the test samples examined, except 4-thiaheptane, its use generally would severely limit the scope of the method. An average value of 0.43 cal/g/°C was therefore used throughout, which represents an average of the heat capacities of fifty-four hydrocarbons, sulphur compounds and alcohols.

The value of c_1g_1 was obtained from experiments on four compounds whose heats of fusion are known. These compounds were chosen to cover a range of 150°C, and were also selected as having heats of fusion not too low for accurate measurement. From the values obtained (Table I) a calibration curve of c_1g_1 against temperature was constructed (Fig. 4).

Using the value of c_1g_1 at the freezing point of the material under examination read from Fig. 4, the heat of fusion can be obtained from equation (2) for both the freezing and melting curves. The average value of these two was used for calculating the cryoscopic constant, using the basic equation (1).

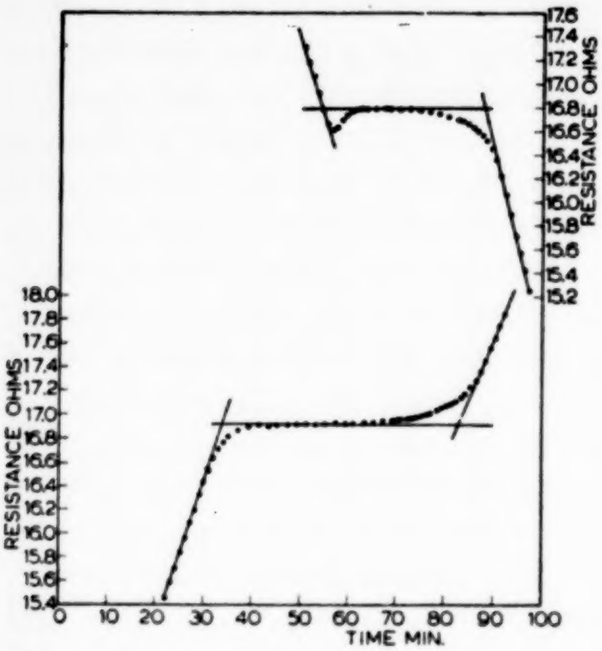

Fig. 3. Freezing and melting curve of ethyl acetate.

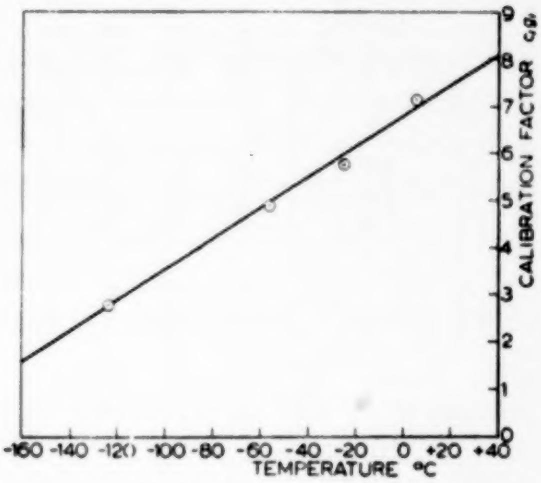

Fig. 4. Calibration factor of apparatus.

RESULTS

The values of the calibration factor c_1g_1 are given in Table I, together with the determined purities of the compounds used in the calibration, the literature values of the freezing point and heat of fusion.

TABLE I

CALIBRATION OF EQUIPMENT

Compound	*Heat of fusion Kcal/mole Lit. value*	*T_{fo} °C Lit. value*	*Average c_1g_1*	*Purity mole %*
2,2-Dimethylpentane	1.392	—123.811	2.79	99.72
n-Octane	4.957	— 56.795	4.89	99.81
Benzene	2.351	+ 5.533	7.16	99.47
o-Xylene	3.250	— 25.182	5.75	99.96

The values of the heat of fusion and freezing point were taken from the Selected Values of Properties of Hydrocarbons and Related Compounds, *API Research Project 44*.

The heats of fusion of the remaining twelve compounds are given in Table II, with the calculated and literature values of the cryoscopic constant.

Finally, in this Table, a comparison is made of the purities obtained by using the literature values for the cryoscopic constant A and also using those calculated by the present method.

DISCUSSION

It was not possible to calibrate the apparatus directly in calories because of the variable conditions under which individual experiments were made. With a fixed pressure in the freezing tube, and with standard cooling and heating baths, it would be possible to make such a calibration[8], but if the pressure in the tube were adjusted such that the time of freeze or melt for compounds with a low heat of fusion would be

TABLE II

EXPERIMENTAL RESULTS

Compound	*T_{fo} °C Lit. value*	*ΔH_{fo} Kcal/mole Lit.value*	*ΔH_{fo} from freezing curve*	*ΔH_{fo} from melting curve*	*Average value H_{fo}*	*Cryoscopic constant Lit.value*	*Cryoscopic constant calculated*	*% Error*	*Purity mole % (Lit.value of A)*	*Purity mole % (calculated A)*	*Reference*
2,4-Dimethylpentane	—119.242	1.636	1.516	1.554	1.535	3.473	3.26	—6.1	99.84	99.85	a
n-Nonane	—53.519	3.697	3.663	4.149	3.906	3.856	4.07	+5.6	99.92	99.92	a
n-Octadecane	+28.180	14.815	13.936	12.860	13.398	8.21	7.42	—9.6	99.25	99.32	a
Cyclopentane	—93.866	0.1455	0.164	0.162	0.163	0.228	0.26	+11.8	99.98	99.98	a
Cyclohexane	+6.554	0.6398	0.754	0.674	0.714	0.411	0.46	+12.2	99.96	99.95	a
3-Methyl-2-thiabutane	—101.51	2.11	2.469	2.165	2.317	3.6	3.96	+9.8	99.93	99.92	a
4-Thiaheptane	—102.6	—	3.169	2.903	3.036	—	5.24	—	—	—	b
Thiophene	—38.21	1.216	1.400	1.396	1.398	1.108	1.27	+14.4	99.93	99.92	a
Thiacyclopentane	—96.16	1.756	1.867	1.940	1.904	2.819	3.06	+8.4	99.86	99.85	c
Thiacyclohexane	+18.99	0.5852	0.667	0.688	0.678	0.345	0.40	+15.9	99.96	99.96	d
Ethyl alcohol	—114.4	1.18	1.179	0.952	1.066	2.38	2.16	—9.6	—	—	e
Ethyl acetate	—83.6	2.505	2.639	2.306	2.473	3.51	3.46	—1.4	—	—	e

(a) Selected Values of Properties of Hydrocarbons and Related Compounds, *API Research Project 44*.
(b) Freezing point determined experimentally.
(c) W. N. Hubbard, H. L. Finke *et al.*, *J. Am. Chem. Soc.*, 74 (1952) 6025.
(d) J. P. McCullough, H. L. Finke *et al.*, *J. Am. Chem. Soc.*, 76 (1954) 2661.
(e) J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing Co. Inc., Amsterdam, 1950.

sufficiently long for accurate measurement, then the time taken for a compound with a high value would be many hours.

From Table II, it will be seen that the error present in the determination of cryoscopic constant ranges from — 9.6% to + 15.9%. The following factors will influence the accuracy of the measured values:

a) Temperature and weight are measured to 0.01°C and ± 0.1 mg respectively, and it can be expected that the small errors which may be present in these quantities will have little effect on the final value. The time of freeze or melt can generally be estimated from the graphs to one or two minutes, but even with the best vacuum obtainable with the system, the time for compounds with a low heat of fusion is such as to cause a reduction in accuracy.
b) The use of the value of 0.43 cal/g/°C for the heat capacity must account for a considerable part of the error involved.

From these considerations, and from the results in Table II, it will be apparent that although the method is not suitable for the precise determination of heat of fusion or cryoscopic constant, it is suitable for use in the evaluation of purity. The inaccuracy present in the value of the cryoscopic constant has little effect when the measured purity of the compound is high.

In normal freezing point experiments, it is not uncommon for supercooling of the liquid to occur. Because it is not possible to promote freezing by standard methods such as the addition of previously-frozen crystals or the insertion of a cold rod, it may not always be possible to produce a satisfactory freezing curve. While this has not been experienced in the present work, a result may be obtained from the melting curve alone, and from Table II, it can be expected that the accuracy of the determined cryoscopic constant would be within ± 25%.

From the results in Table II, it can be estimated that the accuracy of the determined quantity of impurity in the samples is ± 20% for compounds with a heat of fusion lower than 1.5 Kcal/mole, and ± 10% for those compounds with a heat of fusion higher than this value.

ACKNOWLEDGEMENT

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SUMMARY

A simple modification to the apparatus used for the determination of freezing points enables cryoscopic constants to be evaluated. An accuracy of ±10% has been obtained with compounds having a latent heat of fusion greater than 1.4 Kcal/mole, and ±20% below this value. This is sufficiently accurate for most determinations of purity by the freezing point method.

RÉSUMÉ

Une simple modification de l'appareil utilisé pour la détermination de points de congélation permet d'évaluer les constantes cryoscopiques. Une précision de ± 10% a été obtenue pour des composés ayant des chaleurs de fusion latentes supérieures à 1.4 Kcal/mole, et de ± 20% en dessous de cette valeur. Cette précision est suffisante pour la plupart des déterminations de pureté par la méthode des points de congélation.

ZUSAMMENFASSUNG

Eine einfache Modifikation des zur Gefrierpunktsbestimmung benützten Apparates gestattet die Ermittlung der kryoskopischen Konstanten. Eine Genauigkeit von ± 10% wurde für Verbindungen erhalten, deren latente Schmelzwärme grösser als 1.4 Kcal/Mol ist; eine solche von ± 20% unterhalb dieses Wertes. Diese Genauigkeit genügt für die meisten Reinheitsbestimmungen mit Hilfe der Gefrierpunktmethode.

References p. 132

REFERENCES

[1] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, 35 (1945) 355.

[2] B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, 26 (1941) 591.

[3] W. D. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, 32 (1944) 197.

[4] ASTM Standard Method of Test for Measurement of Freezing Points of High Purity Compounds for Evaluation of Purity, *Designation* D 1015-55.

[5] D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *J. Am. Chem. Soc.*, 73 (1951) 3627.

[6] E. V. Whitehead, R. A. Dean and F. A. Fidler, *J. Am. Chem. Soc.*, 73 (1951) 3632.

[7] W. Crawford and C. L. A. Harbourn, *Anal. Chem.*, 27 (1955) 1449.

[8] F. D. Rossini, *J. Research Natl. Bur. Standards*, 11 (1933) 553.

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AN AUTOMATIC ADIABATIC LOW TEMPERATURE CALORIMETER

by

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INTRODUCTION

Since the chemical industry has been applying the thermodynamic approach to its problems with increasing vigor, it became necessary to streamline the equipment used to measure low temperature heat quantities, purity of materials, third law entropies, *etc.* In order to reduce operating manpower, thorough instrumentation of the apparatus was undertaken. Machine control of the variables is an improvement over manual operation and produces a more rapid flow of consistent information. Over ten years ago the problem of making an automatic adiabatic low temperature calorimeter was discussed with several calorimetrists, most of whom expressed the belief that automatic operation was out of the question. This article describes an adiabatic calorimeter for use from 5° to 330°K that will operate by itself around the clock, and produce a record of all pertinent data.

AUTOMATIC CALORIMETRY

An early automatic adiabatic low temperature calorimeter was reported by SOUTHARD AND ANDREWS[19] who employed a difference thermocouple between the sample container and the shield connected to a sensitive mirror galvanometer. A light beam reflected from the mirror onto a photoelectric cell when the shield required heat. The photoelectric cell was linked to a servomechanism which supplied a variable electric current to the shield heater. With this arrangement the shield (environment) followed the temperature of the sample container within a variation of ±0.05°K. The shield contained relatively little mass resulting in small lags in the system. This calorimeter heated the sample continuously.

Later, SOUTHARD AND BRICKWEDDE[20] described an adiabatic low temperature calorimeter with discontinuous heating. Two operators were required for this equipment and because of its accuracy (total errors were about 0.1% above 40°K, while at 14°K they increased to 1% because of thermocouple insensitivity) this type of calorimeter became the standard pattern at the National Bureau of Standards. Improvements were made on this basic type of calorimeter by other investigators[2,3,4,5,7,17,18,23]. (This is by no means an exhaustive list.)

THE CALORIMETER

A scale diagram of the calorimeter which was developed is shown in Fig. 1. The sample container, A, had a volume of 70 ml and was closed by a threaded plug secured with a Teflon gasket. In a central reentrant well was a four lead platinum resistance thermometer, around which were clustered ten reentrant wells containing heaters. The thermometer (R_0 = 93 ohms) consisted of a strain-free bifilar helix wound on a mica framework as described by SOUTHARD AND MILNER[21] and MEYERS[13]. This thermometer was constructed in our own facilities. The replaceable heaters were of constantan wire and had a resistance of 10 ohms each. They were insulated with glass thread over which was drawn a close fitting copper sheath. Intimate thermal contact between the wells and the heaters and thermometer was achieved by application of silicone grease.

Twenty heat distributing discs were metallically bonded to the heater wells but did not touch the outside wall or the thermometer well. Below the sample volume was a false bottom in which the heater and thermometer leads were soldered to copper lugs which protruded beyond the outer wall of the container. External leads to these lugs were unsoldered and resoldered to change samples. Sample containers were constructed of copper joined with tin (complete weight 145 grams), of magnesium joined by arc welding (complete weight 98 grams) and of platinum joined with gold solder (complete weight 261 grams).

The sample container was supported by a copper strip clamped around the middle. The sample thermocouple junctions were secured to, but electrically insulated from this copper strip. Changing the sample thus required unclamping and reclamping of this copper strip. The copper strip hung from three linen threads whose position could be adjusted externally by a windlass as described by RUEHRWEIN AND HUFFMAN[17].

Surrounding the sample container was a thin walled shield, B, made of copper joined with silver solder and weighing 275 grams. The bottom was hinged and provided easy access

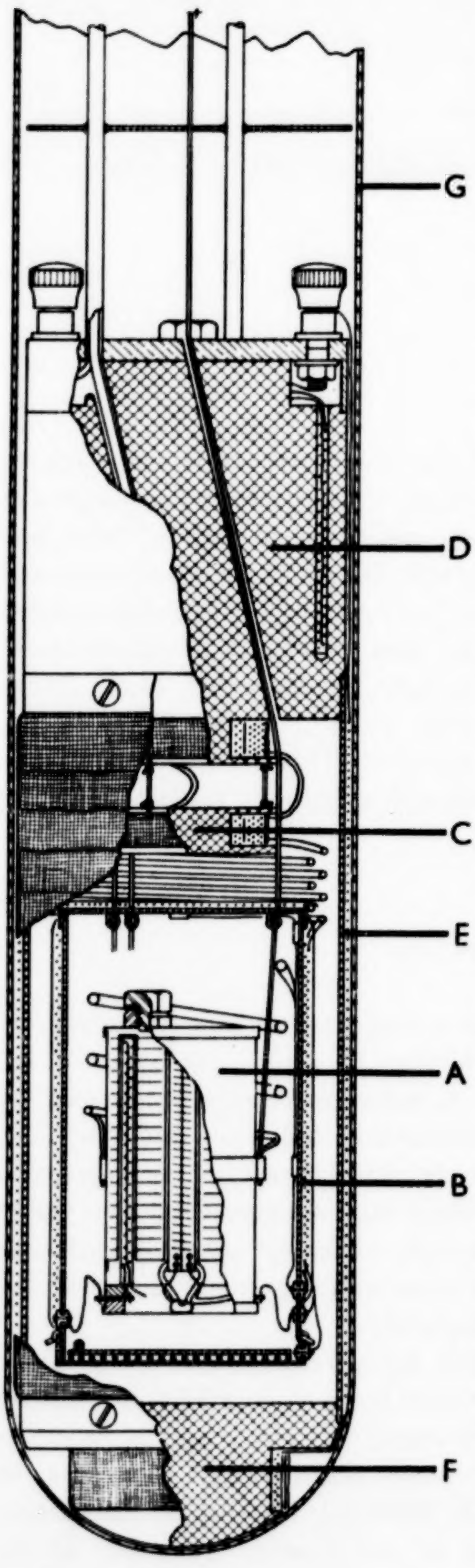

Fig. 1. The calorimeter.

and closure for changing samples. Between the inner wall of the shield and the copper sample support strip there was a twelve junction thermel made of Chromel-P and constantan wire. The remaining thermocouples were made of copper and constantan wire. All wire junctions were made by electric welding, wrapped with glass thread and impregnated with a special electric varnish[9]. All of the wires from the interior of the shield were wound on the outer surface of the shield for three turns and secured with varnish. Separate heaters were wound bifilarly on the top, side and bottom surfaces of the shield. The shield hung by three linen cords from the floating ring, C, which in turn hung by three linen cords from the upper block, D.

The floating ring was a 100 gram spool of copper with a constantan heater and a difference thermocouple having junctions on the floating ring and sample container support strip. All the wires from the shield were wound in intimate contact with the floating ring and secured with varnish. All the wires from the floating ring were wound and varnished to the lower portion of the upper block then passed through holes to the wire chamber at the top of the upper block. From the upper block, the wires passed through monel tubes containing copper discs to the top closure plate where they emerged through a vacuum seal of Pyseal wax.

The environment of the shield consisted of three parts: the upper block, D, the sleeve, E, and the lower block, F. The upper block contained 4,440 grams of copper, replaceable constantan heaters, and a copper constantan control thermocouple whose other junction was on the floating ring. A brass cap silver soldered to three thin walled monel tubes was bolted to the top of the upper block and provided support for the assembly. The sleeve was made of thin walled copper tubing, weighed 427 grams and was fastened to the upper block with screws. The sleeve contained a constantan heater and a copper constantan control thermocouple whose other junction was on the floating ring. The lower block contained 1,160 grams of copper, a constantan heater, a copper constantan control thermocouple whose other junction was on the floating ring, and was fastened to the sleeve with screws. All of the sleeve and lower block lead wires were attached to binding posts at the top of the upper block to facilitate disassembly.

For refrigeration purposes the calorimeter was mounted in the experimental cavity of a Collins Helium Cryostat[1]. The cavity, G, was formed of a stainless steel tube 9.5 centimeters in diameter and 1.25 meters deep with a hemispherical bottom and could be evacuated. It was possible to refrigerate the cavity with liquid nitrogen or liquid helium. The calorimetric assembly was inserted and removed by the hydraulic hoist provided with the cryostat, and was made vacuum tight with "O" rings

CONTROLS

As shown in Fig. 2 a twelve junction Chromel P-constantan thermocouple registered any difference in temperature between the sample container and the shield and was connected directly to a servoamplifier. In this servoamplifier the signal was fed to an indicating microvolt amplifier[12a]; the output of this amplifier was fed to an Electronik amplifier and motor[14a]. This motor operated a microswitch, which controlled the shield heating current.

Provision was made for an adjustable bucking potential to offset the control point from the true null point. When the twelve junction thermel signaled that the shield was colder than the sample container, the servoamplifier switched direct current to the shield heaters. The three shield heaters had external variable series resistors and a common return. At 300°K the sensitivity was such that the shield never differed by more than ± 0.002°K, while at 30°K this difference did not exceed ± 0.012°K. With this type of "on-off" control the temperature of the shield cycled above and below the temperature of the sample container, but by correct positioning of the control point and the heating current the length of time spent "too cold" was made equal to the time spent "too hot". These two effects thus cancelled each other resulting in virtually ideal control of the shield to the temperature of the sample container at all times.

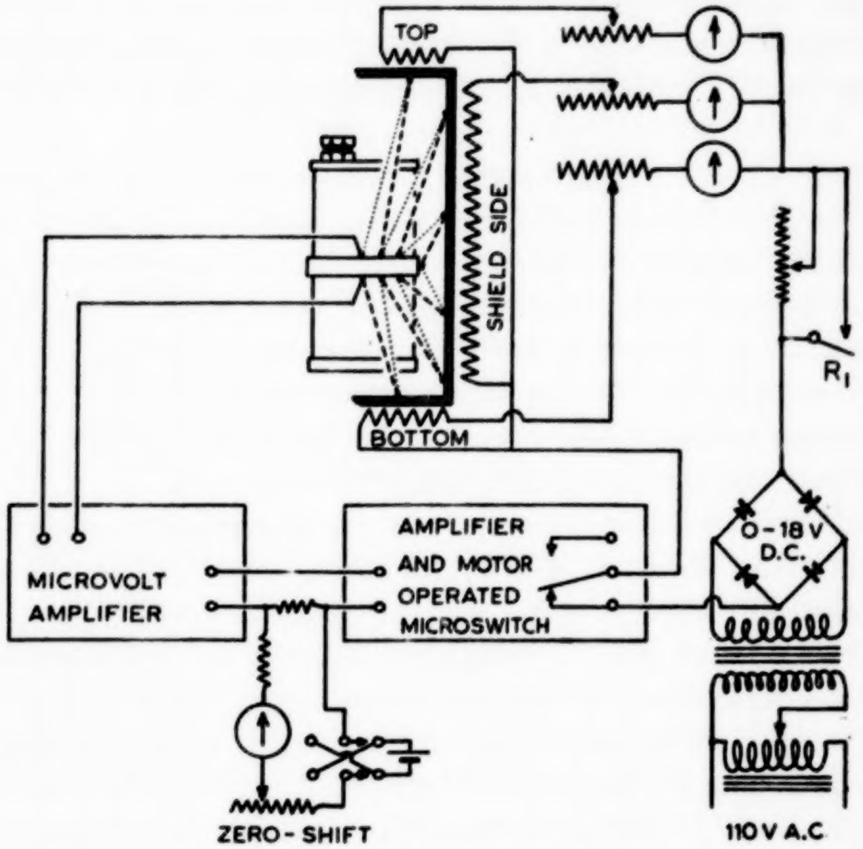

Fig. 2. Shield control circuits.

The single junction copper-constantan thermocouple connected between the sample container and the ring was fed into a servomechanism identical to that described above. This servo-system kept the temperature of the ring the same as that of the sample to within limits that were twelve times as great as noted above, *i.e.* at 300°K about ± 0.024°K and at 30°K about ±0.144°K. Thus, the temperature of all the wires leading to the shield were brought to practically the same temperature as the sample container thereby eliminating heat flow in these wires.

Single junction copper-constantan thermocouples were connected between the ring and (a) the lower block, (b) the sleeve and (c) the upper block. Each of these three differential thermocouples was fed to an Electronik amplifier and motor[14a] operating a microswitch. Provision was made for an adjustable bucking potential to offset each control point so that the temperature of the environment could be controlled a desired increment below that of the ring, shield and sample container. In this way the shield was always subjected to a steady cooling gradient so that its correct temperature could be attained by electrical heating.

The shield heaters were supplied with adjustable rectified direct current of 18 volts maximum. In series with the common return from these heaters was a variable resistor which was automatically shunted out when the sample heater was energized. This device compensated for the difference in load during heating and equilibration. The ring heater had a similar independent current supply. The heaters for the lower block, sleeve and upper block were supplied with adjustable alternating current of 28 volts maximum.

MEASURING CIRCUITS

Fig. 3 is a schematic diagram of the measuring circuits. The platinum resistance thermometer ($R_0 = 93$ ohms) was calibrated from 10° to 350°K by comparison at 43 points with a platinum resistance thermometer calibrated by the National Bureau of Standards, whose temperature scale has been described by HOGE AND BRICKWEDDE[10] and by STIMSON[22].

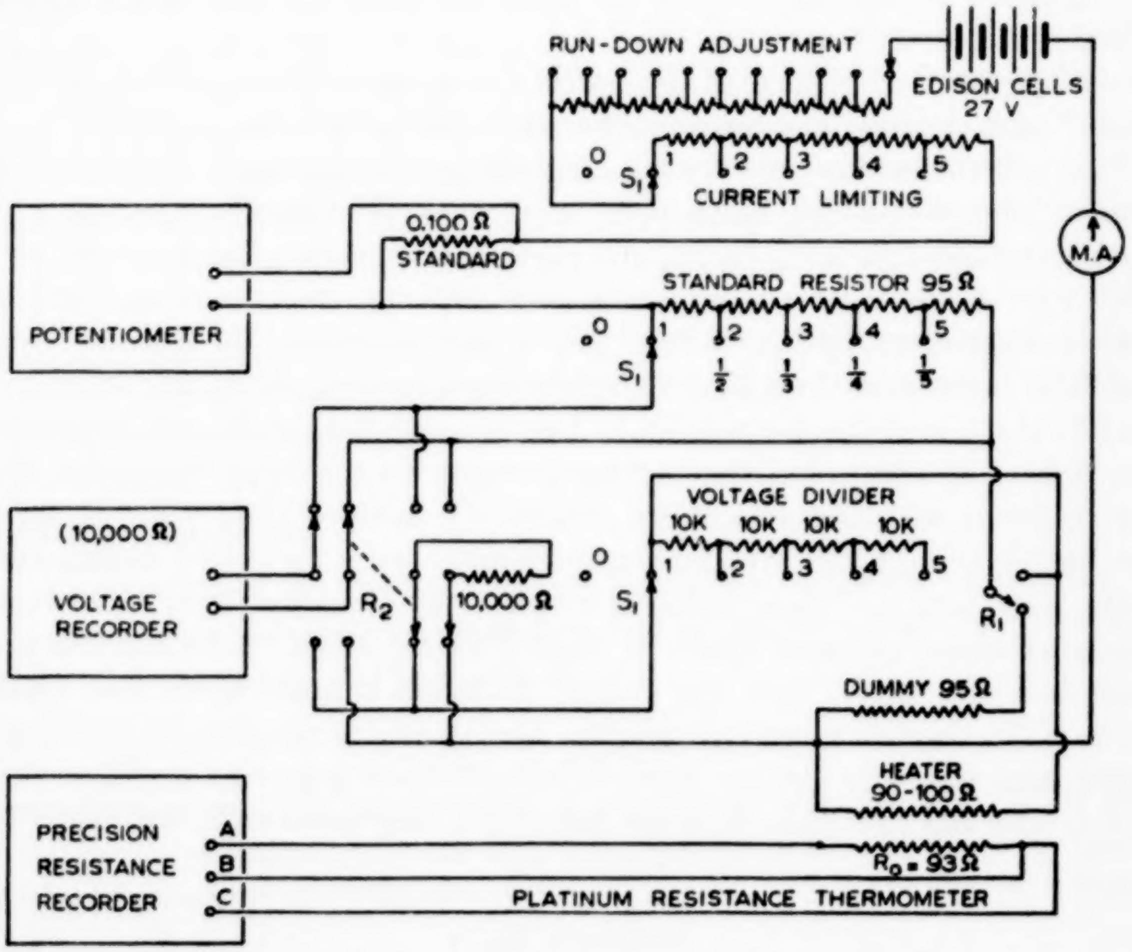
RUN-DOWN ADJUSTMENT
EDISON CELLS 27 V
0
S₁
1
2
3
4
5
CURRENT LIMITING
0.100 Ω STANDARD
M.A.
STANDARD RESISTOR 95 Ω
POTENTIOMETER
0
S₁
1
2
3
4
5
1/2
1/3
1/4
1/5
VOLTAGE DIVIDER
10K
10K
10K
10K
(10,000 Ω)
VOLTAGE RECORDER
R₂
10,000 Ω
0
S₁
1
2
3
4
5
R₁
DUMMY 95 Ω
HEATER 90-100 Ω
PRECISION RESISTANCE RECORDER
A
B
C
R₀ = 93 Ω
PLATINUM RESISTANCE THERMOMETER

Fig. 3. Temperature and power measuring circuits.

The resistance of the platinum thermometer in the sample container was recorded continuously on a "High Precision" resistance recorder[12b]. With this equipment the temperature of the sample at 300°K could be read to ±0.0028° while at 30°K this was ±0.0058°. Since the temperature of the sample and its container were recorded continuously, transitions or specific heat anomalies were readily observed on the time-temperature curve.

The ten replaceable heaters in the sample container were surrounded by the sample and were about midway between the platinum resistance thermometer (center) and the outer wall. The series resistance of these heaters at 300°K was 100 ohms and at 5°K about 90 ohms. Current for the heaters was supplied by twelve Edison Storage batteries connected to give 600 ampere hours at 27 volts. This capacity was remarkably stable. A master selector switch S_1 controlled fixed resistors so that the voltage at the heater terminals had the values $n(2.10 \pm 0.10)$ volts, where $n = 1,2,3,4,5$. A series decade box compensated for battery drain and required adjustment about once a week.

The battery was kept on a steady drain by connecting it to a "dummy heater" of 95 ohms, when the sample heater was not energized. A pendulum operated clock[11], monitored by a quartz crystal controlled oscillator, and periodically checked against the signal sent out by radio station WWV, was used to time the duration of the heat inputs as well as the time between the heat inputs. These intervals of time were accurate to 0.01 sec or better. Several different timing schedules were available and could be operated continuously. When the heat was on, a continuous 110 A.C. signal originated at the clock which was used to operate relays and which we will collectively refer to as R_1.

The voltage at the terminals of the heater was measured by an Electronik voltage recorder[14b] with a range of 2.000 to 2.200 volts and which was accurate to ±0.002 volts. This instrument had an internal resistance of 10,000 ohms. Ganged to S_1 were four 10,000 ohm resistors connected in series with the recorder forming a voltage divider having the values $^1/_2$, $^1/_3$, $^1/_4$ and $^1/_5$ to accommodate the five voltage levels. In series with the heating circuit was a large capacity manganin standard resistor of 95 ohms tapped at $^1/_2$, $^1/_3$, $^1/_4$ and $^1/_5$ and also ganged to the selector switch S_1. For one heat input and the following equilibration period, R_1 connected the voltage recorder to the sample heater terminals. For the next heat input and ensuing equilibration period R_1 connected the voltage recorder to the large manganin standard resistor in series with the sample (or "dummy") heater. Thus, the voltage of the sample heater and of the standard series resistor were measured continuously on alternate heat inputs. These voltages changed in a regular manner so that intermediate unrecorded voltages could be readily interpolated. A 10,000 ohm resistor was switched alternately into the voltage leads not connected to the voltage recorder to make conditions as reproducible and steady as possible. All of this periodic switching was done by rotary type switches[12c] having contact resistance less than 0.001 ohm, thermal e.m.f. less than one microvolt, and electrically driven by R_1.

SPECIFIC HEAT

(a) Method of measurement

After placing the sample in the sample container, the closure was fastened and the sample weighed. After two hours in an evacuated dessicator, reweighing checked the tightness of the closure. After assembly the cryostat was evacuated and filled with helium gas. Liquid nitrogen was automatically added so that the surroundings were maintained 20° colder than the sample. In 5 or 6 hours, the sample had cooled to 100°K, while the resistance thermometer recorder had drawn a cooling curve, which included the transitions or phase changes that were encountered. The helium liquifier was started and in 3 to 4 hours the sample had cooled to about 5°K.

The diffusion pumps were started, and the servomechanisms energized. As the helium was pumped out, there came a time when the sample temperature developed a drift to a higher temperature. This occurred when the pressure of the helium reached about 10^{-3} mm of mercury. When this upward drift had begun, heat inputs to the sample were started. These were of such magnitude and duration that the sample temperature increased about 5 degrees per heat input. The rate of addition could be varied from about 3 degrees per minute to 0.05 degrees per minute. The usual rate was about 0.1 degrees per minute. After a heat input the temperature of the sample approached a constant value as the heat was equilibrated in the sample and its container. This drop in temperature was 0.2 degrees or less. Under usual operating conditions, the vacuum was 2×10^{-5} mm of mercury or better.

When the sample temperature reached 35° or 40°K, the helium liquifier was stopped since there was sufficient refrigeration capacity within the cryostat to insure that the sample and its shields would be able to warm faster than the rest of the equipment. There was no observable effect on the calorimeter due to the operation of the liquifier. A low lying melting point or transition sometimes required additional liquid nitrogen refrigeration. In 75 to 100 hours, the sample had warmed to 320° to 350°K and the run was terminated. The only human attention required was to change the heat level switch or to occasionally (2 or 3 times during the 8 hour working day) readjust the controls. While a run was in progress, the operator had ample time to inspect the records of the previous run, and compile a set of tabular values for the calculations.

Additional runs were made on the empty container, and were identical in every way except that the container was filled with about 0.5 atmosphere of helium gas to promote temperature equilibration.

(b) Method of calculation

During a heat input, an electric current of I amperes flowed through the sample heater because of a voltage e impressed on the heater terminals for t seconds. The heat in calories developed in the heater is

$$H = \frac{Iet}{4.1840} \quad \text{(1)}$$

This heat input caused the temperature of the sample to go from its initial value T_i before the heat was added to T_f the final temperature of the sample after the sample had reached a constant temperature. Thus, $T_f - T_i = \triangle T$ the rise in temperature due to H, and $\frac{T_f + T_i}{2} = T_a$ the average temperature of the heat input.

Now H was absorbed by the sample container of weight w grams and specific heat c_{p_c} at T_a as well as by the sample of W grams and specific heat c_{p_s} at T_a. This was expressed mathematically as:

$$H = [wc_{p_c} + Wc_{p_s}] \triangle T \quad \text{(2)}$$

combining equations (1) and (2) gave

$$\frac{Iet}{4.1840\ W\triangle T} - \frac{w}{W} c_{p_c} = c_{p_s} \quad \text{(3)}$$

which was the basic equation used to calculate the heat capacity of the sample. Calculations were made by a high speed electronic calculator[6]. The following values were supplied to the computer: e_c the voltage at the sample heater terminals, e_r the voltage across the series standard resistor, R_i the platinum thermometer resistance at T_i, R_f the platinum thermometer resistance at T_f, t the duration of the heat input in seconds, w the weight of the sample container, W the weight of the sample, the number of the container and the number of the platinum resistance thermometer. e_c and e_r were corrected for the current through the recorder. Tables of R, the thermometer resistance, *vs.* T and of c_{p_c} *vs.* T were searched by the computer to convert R_i to T_i, R_f to T_f and from T_a to find c_{p_c}. Next from the known value of the resistance of the standard series resistor R_r the current through the heater was calculated.

$$I = \frac{e_r}{R_r} \qquad (4)$$

Combining with equation (3) gave

$$\frac{e_r\, e_c\, t}{4.1840\, R_r\, W \Delta T} - \frac{w}{W} c_{p_c} = c_{p_s} \qquad (5)$$

Equation (5) was used to convert the data from each heat input to a value of c_{p_s} at T_a.

(c) Results

In order to verify the performance of this apparatus, the thermal properties of *n*-heptane were measured from 5° to 310°K. The *n*-heptane was obtained from the National Bureau of Standards and was a portion of that certified as a heat capacity standard[8]. Additional measurements of the heat capacity of *n*-heptane have been reported by the Petroleum Experiment Station, U. S. Bureau of Mines, by PARKS, HUFFMAN AND THOMAS[15], and by PITZER[16]. In Fig. 4 these four sets of measurements are compared with those of DOUGLAS, FURUKAWA, MCCOSKEY AND BALL[8] by plotting the percentage deviation of the measurements from those made at the National Bureau of Standards. Examination of these data indicated that the greatest divergen-

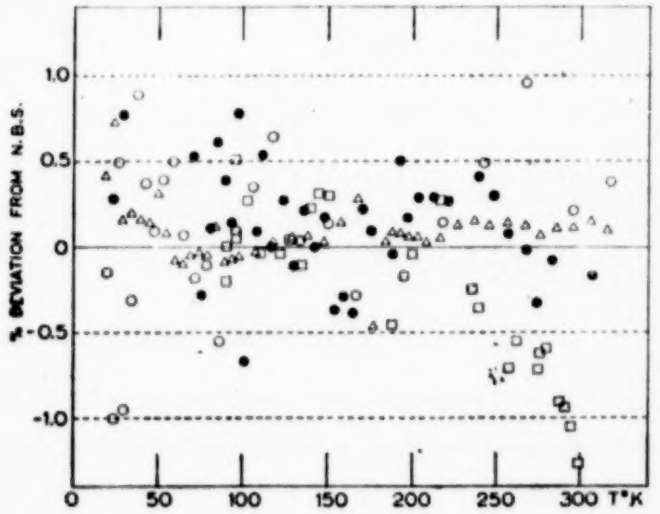

Fig. 4. Comparison of data on *n*-heptane.
△ U.S. Bureau of Mines
☐ PARKS, HUFFMAN AND THOMAS[15]
○ PITZER[16]
● This report

ce was at temperatures below 90°K. This was thought to be due in part to the temperature scale uncertainties that exist in this region, and also to the insensitivity of equipment and experimental difficulty in this range. It will be noticed (see our points at 100°K) that sometimes a high point was followed by a low point. This was thought to be due to too short an equilibration time of one measurement resulting in an incorrect equilibrium temperature. It was further noticed that the scatter of the points was random, and above 100°K all the points fell within ± 0.5% and most of them were within ± 0.3%. This became more apparent when a best curve was passed through the data and the deviation of the experimental points from this smooth curve were plotted in Fig. 5.

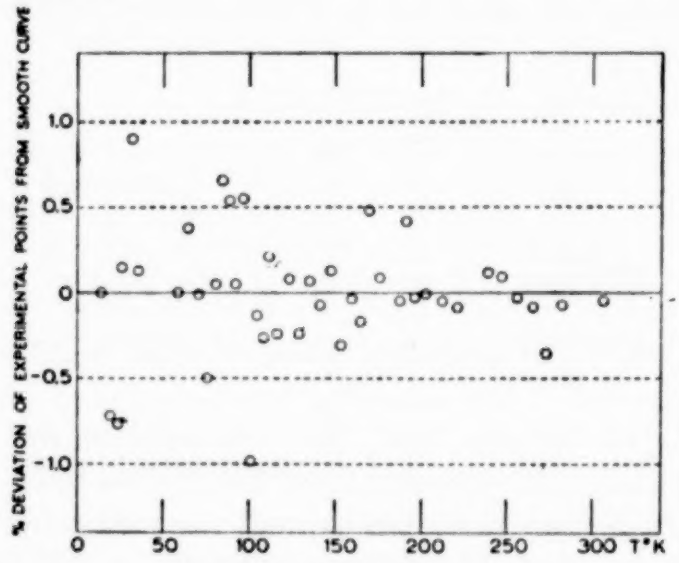

Fig. 5. *n*-Heptane.

HEAT OF PHASE CHANGE

(a) Method of measurement

When a phase change occurred with this apparatus, $\triangle T$ diminished and toward the last part of the process became nearly zero. c_{p_c} was known through this region and c_{p_s} was extrapolated through any premelting that may have taken place. The remainder of H was taken up by the phase change. Thus,

$$H - [wc_{p_c} + Wc_{p_s}]\,\triangle T = \triangle H_m \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where $\triangle H_m$ was an increment in the heat change associated with the phase change. When the phase change was complete all of the $\triangle H_m$ were summed and the fraction of the sample which had undergone the phase change with each heat input was computed.

(b) Results

Three determinations of the heat of melting of *n*-heptane at different rates gave the following values:

Run	*Molal heat of melting*
1	3352.7 cal
2	3358.1
3	3361.3
Average	3357.4 ± 4
N.B.S.[8]	3351.5 ± 2
PITZER[16]	3356 ± 4
P.H. AND T.[15]	3385

References p. 143

Experimental work has proven that the heat of melting value is independent of the rate of heat input.

CALCULATED PURITY

The run which was selected for this report contained eleven heat inputs for the melting process. Each heat input was 60 minutes long followed by an equilibration period of 30 minutes. Thus, the melting process extended over 16.5 hours. Fig. 6 shows an analysis of the melting data; the reciprocal of the fraction melted was plotted against the equilibrium temperature. From this data the triple point was 182.54°K (using 273.16°K for the ice point), and the purity of the sample was 99.98 mole per cent. N.B.S. reported the triple point at 182.562°K for a sample of 99.999 ± 0.002 mole % purity. The purity of the sample from these measurements is not as high as that reported by N.B.S. since the sample was transferred in air and may have absorbed some moisture.

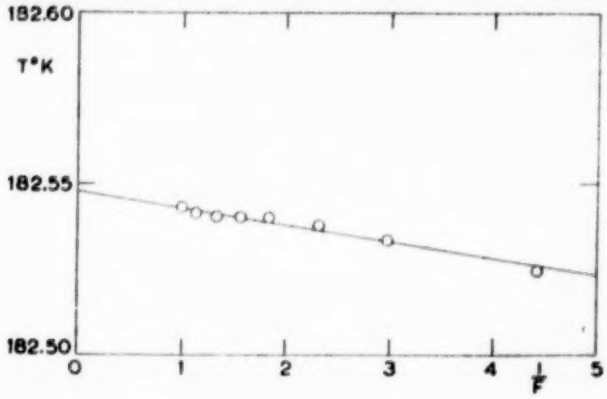

Fig. 6. Melting of *n*-heptane, where *F* is the fraction melted.

CONCLUSION

The results obtained with this automatic equipment compare favorably with the average of all the measurements on *n*-heptane reported in the literature. These measurements were among the first made with the equipment described; further improvement will result from additional experience and redesign. The agreement between these measurements and those of other investigators indicate that this equipment is adequate for third law studies, and for purity determinations.

ACKNOWLEDGEMENT

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SUMMARY

The calorimeter, for use at temperatures from 5° to 330°K, has several novel features. Servo-loops have been developed that will maintain the sample environment at a temperature virtually the same as the sample container. All factors necessary for calculation of the results are controlled and recorded automatically as a function of time. Results on *n*-heptane are presented and serve to establish the reliability of this equipment.

References p. 143

RÉSUMÉ

L'auteur décrit un calorimètre pour des températures allant de 5°K à 330°K qui présente plusieurs caractères nouveaux. Des dispositifs automatiques maintiennent l'environnement de l'échantillon à une température virtuellement égale à celle du contenant de l'échantillon. Tous les facteurs nécessaires pour le calcul des résultats sont réglés et enregistrés automatiquement en fonction du temps. L'auteur présente les résultats obtenus avec le *n*-heptane; ils établissent la bonne qualité de cet équipement.

ZUSAMMENFASSUNG

Das hier beschriebene Kalorimeter, für Temperaturen zwischen 5°K und330°K, hat verschiedene neue Merkmale. Es wurden automatische Systeme entwickelt, welche die Umgebung der Probe auf virtuell derselben Temperatur halten, wie den Behälter der Probe. Alle zur Berechnung der Ergebnisse notwendigen Faktoren werden automatisch reguliert und als Funktion der Zeit registriert. Die mit *n*-Heptan erhaltenen Resultate werden mitgeteilt; sie beweisen die Verlässlichkeit dieser Ausstattung.

REFERENCES

[1] Arthur D. Little, Inc., of Cambridge, Mass., U.S.A., Manufacturer of the Collins Cryostat.

[2] J. G. Aston and M. L. Edinoff, *J. Am. Chem. Soc.*, 61 (1939) 1533.

[3] J. G. Aston, H. L. Finke, G. J. Janz and K. E. Russel, *J. Am. Chem. Soc.*, 73 (1951) 1939.

[4] J. G. Aston and C. W. Ziemer, *J. Am. Chem. Soc.* 68 (1946) 1405.

[5] R. W. Blue and J. F. G. Hicks, Jr., *J. Am. Chem. Soc.*, 59 (1937) 1962.

[6] Burroughs Corp., Electrodata Division, 460 Sierra Madre Villa, Pasadena, Calif., U.S.A.

[7] T. M. Dauphinee, D. K. C. MacDonald and H. Preston-Thomas, *Proc. Roy. Soc. (London)*, A221 (1954) 267.

[8] T. B. Douglas, G. T. Furukawa, R. E. McCoskey and A. F. Ball, *J. Research Natl. Bur. Standards*, 53 (1954) 139.

[9] General Electric Company, Schenectady, N.Y., U.S.A. This varnish is known as No. 7031 adhesive.

[10] H. Hoge and G. G. Brickwedde, *J. Research Natl. Bur. Standards*, 22 (1939) 351.

[11] International Business Machines Corp., 590 Madison Ave., New York 22, N.Y. Master clock, Sub-master Control Unit, and Program Unit.

[12] Leeds and Northrup Co., 4901 Stenton Ave., Philadelphia 44, Pa., U.S.A.
(a) Catalog No. 9835-B.
(b) Catalog No. 69812.
(c) Type 31-3 Selector Switch.

[13] C. H. Meyers, *J. Research Natl. Bur. Standards*, 9 (1932) 807.

[14] Minneapolis Honeywell Regulator Co., Brown Instrument Division, Wayne and Windrum Aves., Philadelphia 44, Pa., U.S.A.
(a) Part. No. 356358-1 and No. 76750-3.
(b) Type 153, Model Y153X12(X)-X-(6)(V), Electronik Strip Chart Recorder.

[15] G. S. Parks, H. M. Huffman and S. B. Thomas, *J. Am. Chem. Soc.*, 52 (1930) 1032.

[16] K. S. Pitzer, *J. Am. Chem. Soc.*, 62 (1940) 1224.

[17] R. A. Ruehrwein and H. M. Huffman, *J. Am. Chem. Soc.*, 65 (1943) 1620.

[18] R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde and N. Bekkedahl, *J. Research Natl. Bur. Standards*, 35 (1945) 39-85.

[19] J. C. Southard and D. H. Andrews, *J. Franklin Institute*, 208 (1930) 349.

[20] J. C. Southard and F. G. Brickwedde, *J. Am. Chem. Soc.*, 55 (1933) 4378.

[21] J. C. Southard and R. T. Milner, *J. Am. Chem. Soc.*, 55 (1933) 4384.

[22] H. F. Stimson, *J. Research Natl. Bur. Standards*, 42 (1949) 209.

[23] D. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, Jr., *J. Am. Chem. Soc.*, 63 (1941) 3488.

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A SIMPLIFIED CALORIMETER FOR THE PRECISE DETERMINATION OF PURITY[1]

by

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I. INTRODUCTION

The purity of organic compounds must generally be established by physical methods, the most widely applicable of which is to compare the freezing point of the actual sample with the value for zero impurity. The accurate determination of freezing points by time-temperature analysis has been developed and has been extensively used by the American Petroleum Institute Research Project 6 for the determination of the purities of hydrocarbon samples. Also, methods have been developed for determining the cryoscopic constant A[1,2]. The extrapolation procedures for determining the freezing point for zero impurity have been described[3]. The time-temperature method yields an accurate and precise value for the freezing point of the actual sample. The method does not yield a comparatively precise value of the freezing point for zero impurity because of the extrapolation involved and the assumption of a uniform rate of heat input by stirring. Hence, particularly for highly purified samples, the precision of measurement of the amount of impurity is generally less than desired. Another time-temperature method for determination of purity is that of SCHWAB AND WICHERS[4] but for this it is necessary to add a known amount of impurity to the sample. This is a great disadvantage in measuring highly purified samples because the purity of the sample is destroyed.

The calorimetric method for the determination of purity involves measurement of the temperature of solid-liquid equilibrium as a function of the fraction of the sample melted. The advantages of the calorimetric method over the time-temperature methods are that greater precision is obtained in determining the difference between the freezing point of the actual sample and that for zero impurity; and that the amount of impurity, the heat of fusion and thus the cryoscopic constant, are all determined from the same experiment. The freezing point of the actual sample and hence that for zero impurity may be determined with a precision equal to that of the most successful time-temperature experiments; that is to within one or two thousandths of a degree C. The time-temperature method has been most extensively used for measuring freezing points in air at 1 atmosphere pressure whereas the calorimetric method is generally used for measuring the freezing point at the saturation vapor pressure of the compound, *i.e.* the triple point.

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[1] This investigation was performed under the American Petroleum Institute Research Project 6 in the *Petroleum Research Laboratory at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania.*

II. THEORY

The theory of the method has been described by ROSSINI[5]. The thermodynamic relation for equilibrium between a liquid phase, of the major and minor components, and a crystalline phase of the major component alone is given by:

$$\ln N_1 = \ln(1-N_2) = -A(T_1^* - T)\,[1 + B(T_1^* - T) + \ldots] \qquad (1)$$

where N_1 and N_2 are the mole fractions of the major and minor components respectively, in the liquid phase. T is the temperature of equilibrium and T_1^* is the temperature for $N_1 = 1$, *i.e.*, the freezing point of the major component with zero impurity. A and B are the first and second cryoscopic constants respectively, given by:

$$A = \Delta Hm/RT_1^{*2} \text{ and } B = (1/T_1^*) - \Delta Cp/2\Delta Hm$$

where $\triangle Hm$ is the molar heat of fusion of the major component and $\triangle Cp$ is the molar heat capacity of the liquid less that of the solid.

For highly purified samples, T approaches T_1^* and N_2 approaches zero so that (1) may be written,

$$N_2 = A(T_1^* - T) \qquad (2)$$

If T_1^* is known in terms of the same thermometric system used to determine the actual freezing point of the sample, T^s, *i.e.* that temperature for which an infinitesimal quantity of crystals is in equilibrium with the liquid; then measurement of T^s can be used to determine N_2^s, the mole fraction of impurity in the sample.

If N_2 is the mole fraction of impurity in the liquid phase for a fraction r of the sample liquid, then;

$$N_2 = N_2^s(1/r) \qquad (3)$$

Combination of (2) and (3) gives;

$$T = T_1^* - (N_2^s/A)(1/r) \qquad (4)$$

A plot of T against $(1/r)$ will give a straight line of slope $-(N_2^s/A)$ and the intercept at $(1/r) = 0$ will be T_1^*. From the slope of the line, the purity of the sample is determined.

The physical assumptions are that the ideal solution laws are obeyed and that the impurity is liquid-soluble, solid-insoluble. The ideal solution law is applicable for small amounts of impurity but solid solution can occur when the molecular size and shape of the impurity is similar to that of the major component or when the major component has a small heat of fusion.

If solid solutions are formed, the concentration of impurity in the liquid phase will be less than that given by equation (2) and the corresponding equilibrium temperature will be too high. This will result in an upward concave curvature in the plot of T against $(1/r)$. A treatment has been given by MASTRANGELO AND DORNTE[6] which can be used to obtain the freezing point for zero impurity in such cases.

There is however, a common misconception that concave curvature upwards in the plot of T against $(1/r)$ is always due to solid solution formation; but it has been experimentally demonstrated in this work that curvature can be obtained where solid solutions are not formed. In Fig. 1, two triple point curves of T against $(1/r)$ are shown for *n*-hexadecane, one is linear and the other shows curvature. In the latter case, although steady temperatures were measured, they could not have been equilibrium temperatures; and in these two experiments there was presumably a difference in the course of melting. In Fig. 2, two curves are shown for cyclohexylcyclohexane and the curvature in the case of the sample exposed to one atmosphere pressure of air is presumably due to only partial saturation of the liquid phase with air. Curvature of the plot of T against $(1/r)$ for measurements in air has therefore no great significance. Thus concave curvature upwards is not conclusive evidence that solid solution occurs and it is important to establish that equilibrium temperatures are measured.

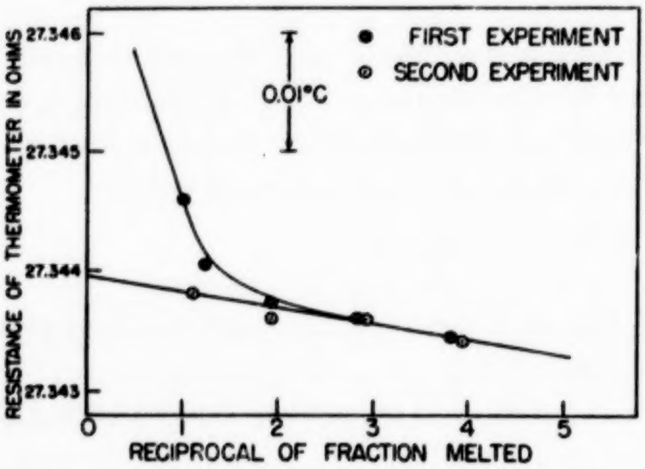

Fig. 1. Curves of fusion data for two triple point determinations on *n*-hexadecane.

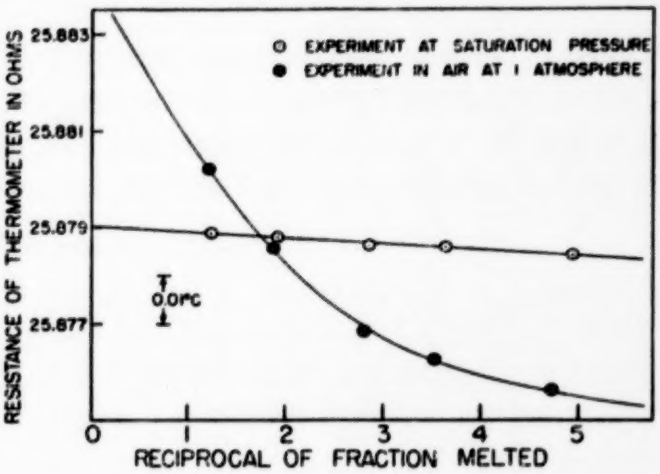

Fig. 2. Curve of fusion data at saturation vapor pressure and in air at one atmosphere on cyclohexylcyclohexane.

The determination of purities from premelting heat capacities has been described by JOHNSTON AND GIAUQUE[7]. This is a method of great sensitivity, up to 0.0001 mole per cent of impurity, but it has not been used in this work because of the large number of heat capacity determinations which are necessary.

III. AIM OF THE PRESENT INVESTIGATION

A simplified calorimeter for the precise determination of purity is described in this report. The need for such an apparatus is perhaps reflected by the description of three such calorimeters in recent years. That of ASTON, FINK, TOOKE AND CINES[8] is a slightly simplified version of the precise low temperature calorimeters but this apparatus is more complex than desired. That of TUNNICLIFF AND STONE[9] is simple to operate but the results are of low precision, the measurements done in air and only compounds melting above —100°C can be examined. That of CLARKE, JOHNSTON AND DE SORBO[10] is suitable for gases but not for liquids and solids.

The main advantages of the apparatus described in this report are that it is simple to operate and has given results of good precision over a temperature range of —170°C to +100°C. If necessary, the upper limit of this temperature range can be extended.

IV. DESCRIPTION OF THE APPARATUS

1. The calorimeter assembly

The calorimeter vessel (Fig. 3) has an internal volume of 44 ml and is generally filled with 35 ml of hydrocarbon measured at room temperature. It is made of copper (0.03 inches thickness), electroplated with gold. The horizontal vanes are to promote thermal equilibrium and to prevent solid falling to the bottom of the calorimeter during the melting period. Holes have been punched in the vanes to permit the introduction of narrow filling tubes and the seeding rod, and also to allow the passage of liquid. Temperature is measured with a platinum resistance thermometer (Leeds and Northrup, Type 8164), set into a central re-entrant well with thermal contact being made by a layer of Apiezon grease. The calorimeter heater (108 ohms, 38 B and S gauge manganin wire) is non-inductively wound round the outside of the calorimeter; the current and potential leads are connected midway between the calorimeter and the adiabatic shield. The thermocouples for adiabatic control are insulated with Teflon sheets (0.01 inches thickness) from the heater and from the outer copper radiation reflector sheath. The calorimeter is supported by the thin walled monel metal tube attached to the main filling tube; monel metal being chosen because of its relatively poor heat conductivity.

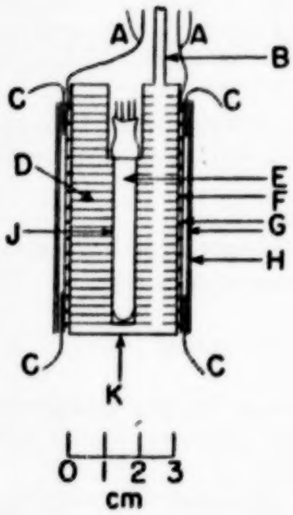

Fig. 3. Calorimeter.

A	current and potential leads to heater
B	thin walled "monel" filling tube
C	thermopile connections (only four are shown)
D	copper vanes (0.007″ thickness) soldered to thermometer well
E	platinum resistance thermometer (Leeds and Northrup Type 8164)
F	heater: 108 Ω: 38 B and S gauge manganin wound directly on calorimeter
G	Teflon insulation (0.01″ thickness) to insulate heater and thermocouples
H	radiation reflector sheath of copper foil (0.007″ thickness)
J	thermal contact between thermometer and calorimeter: Apiezon grease L
K	calorimeter vessel: 0.03″ copper completely covered with gold plate

The complete calorimetric assembly is shown in Fig. 4. An average integrated temperature difference between the calorimeter and the adiabatic shield is measured with a 30 junction thermopile of chromel (28 B and S gauge) and constantan (30 B and S gauge); the junctions being placed as symmetrically as possible. The adiabatic shield is made of copper (1/16 inches thickness) and the shield heater of 20 ohms (made up of four 100 ohms non-inductive windings in parallel) is wound so that the resistance on each part of the shield is directly proportional to the heat capacity of that part. In this way, approximately uniform temperatures are obtained. All the electrical leads from the calorimeter and shield are placed beneath the heater, wound around the filling tube, and are insulated from this heater by Teflon sheet. The

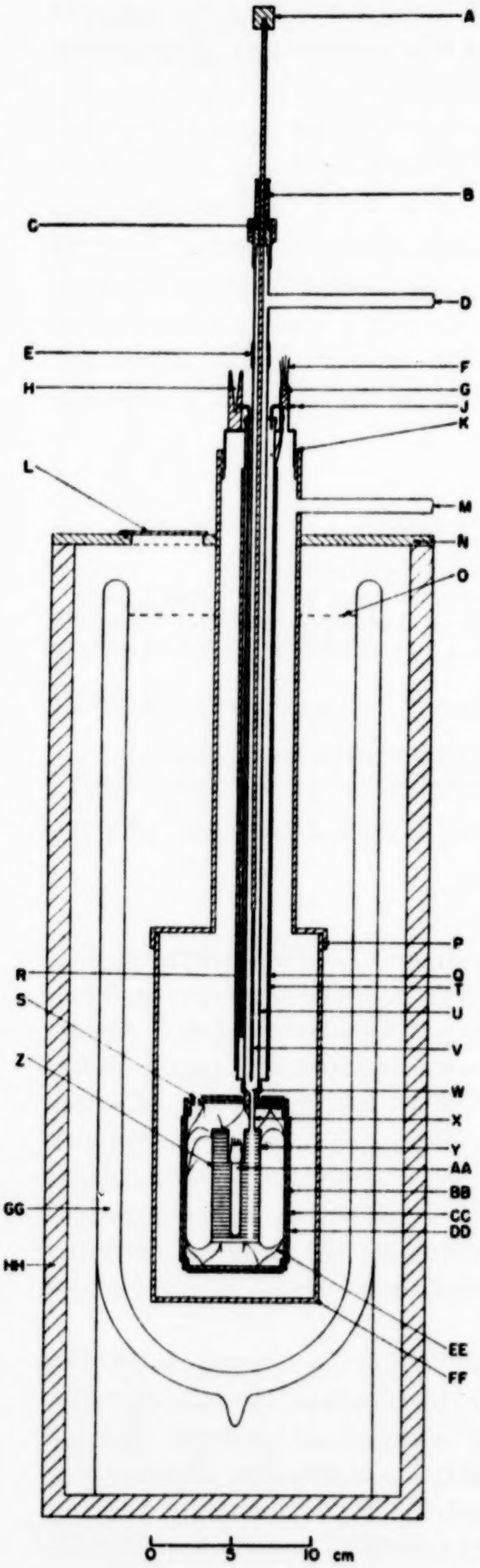

Fig. 4. Complete calorimetric apparatus.

A	knob for controlling seeding rod
B	sliding O-ring vacuum seal for seeding rod
C	O-ring coupling (Cenco Scientific Company)
D	connection to vacuum line for calorimeter vessel
E	monel metal connector
F	the outlet for the electrical leads of the entire system
G	Beeswax-Rosin mixture to seal the electrical leads through a vacuum tight joint
H	inlet for liquid nitrogen for cooling seeding rod
J	outlet for liquid nitrogen for cooling seeding rod
K	soft-soldered joint
L	inlet port for cooling bath with cover
M	connection to vacuum line for jacket of calorimeter
N	1/4'' brass plate: support for the apparatus
O	level of cooling bath
P	Bismuth-solder joint (all other joints except K are hard-soldered)
Q	tube heater with Teflon insulation. All the electrical leads to the calorimeter and the adiabatic shield are placed beneath the tube heater
R	tube for delivery of liquid nitrogen for cooling seeding rod
S	opening in adiabatic shield to permit evacuation of the space between the shield and the calorimeter
T	brass tube to contain liquid nitrogen for cooling seeding rod
U	3/8'' monel metal filling tube
V	seeding rod with wire attached (monel)
W	valve seating to seal off calorimeter. Separate valve replaces seeding rod
X	thin walled monel metal filling tube to calorimeter
Y	calorimeter vessel (copper 0.03'' thickness; completely covered with gold plate)
Z	copper vanes (0.007'' thickness) inside calorimeter
AA	platinum resistance thermometer (Leeds and Northrup No. 8164)
BB	adiabatic shield (copper 1/16'' thickness)
CC	adiabatic shield heater
DD	Teflon sheet insulation and copper foil radiation reflector
EE	chromel-constantan thermocouples (only parts of the distribution of the 30 junctions is shown)
FF	outer container (brass 1/8'' thickness)
GG	Dewar vessel to contain cooling bath
HH	wooden box to contain calorimetric assembly

heater for the filling tube is in series with the adiabatic shield heater and the windings have been adjusted so that the temperature at the bottom of the filling tube will be approximately equal to that of the adiabatic shield. Thus heat conduction down the leads is minimized. The upper part of the tube is kept hotter than the shield to prevent distillation of the compound.

A seeding device is provided. Cold shock seeding can be done by cooling the seeding rod, with liquid nitrogen around the filling tube, and plunging the rod into the sample held at a few degrees C below its melting point. Seeding with crystals can be done by attaching crystals, formed outside of the system, to the end of the seeding rod, keeping them cool with liquid nitrogen around the filling tube and then plunging them into the sample when desired. The seeding rod passes through a sliding vacuum-tight O-ring seal. The O-rings used are of a hydrocarbon resistant rubber material.

For compounds melting above room temperature, the calorimeter can be sealed at the position of the adiabatic shield by a conical valve which is attached to a rod used in place of the seeding rod. This is to prevent distillation of the compound into the vacuum system.

The outer jacket of the calorimeter is made of brass (1/8 inches thickness) and the main seal is of a special solder (41 per cent bismuth, 15 per cent tin, 44 per cent lead)

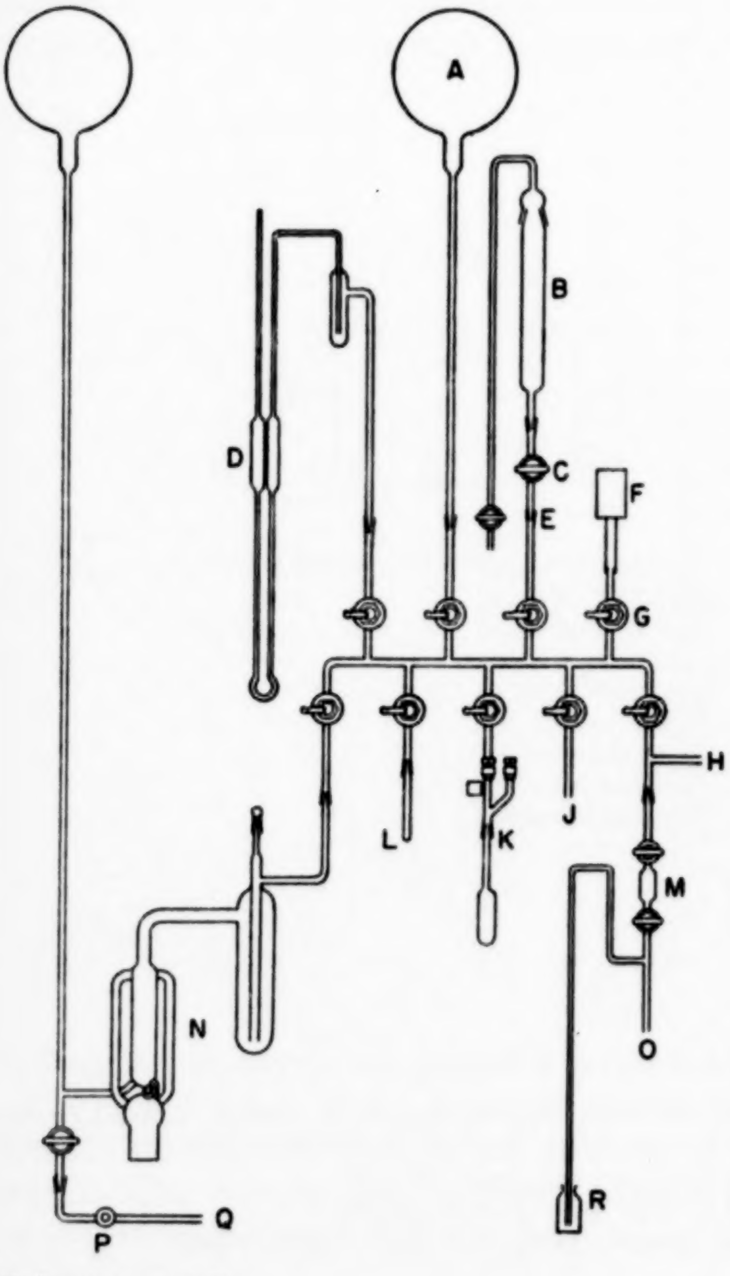

Fig. 5. Vacuum system

A	liter flask for use in degassing samples of hydrocarbons
B	drying tube for admission of dry air to the system
C	glass stopcock
D	mercury manometer
E	metal-glass standard taper soldered connections
F	Philips Vacuum Gauge (25-0.02 microns)
G	stainless-steel diaphragm valves operated by levers (Hoke)
H	connection to calorimeter jacket
J	connection to calorimeter
K	ampoule for distilling hydrocarbons into the calorimeter
L	connection for sealing glass ampoules
M	fixed volume for admission of helium gas to the jacket
N	mercury diffusion pump with trap
O	inlet for helium gas
P	air inlet valve (Cenco O-ring valve)
Q	connection to mechanical rotary pump
R	mercury blow-off for helium inlet system

chosen because it does not crack at liquid nitrogen temperatures. The calorimeter and the jacket are connected through separate valves to the vacuum system.

The cooling bath is placed in the Dewar vessel around the outer jacket. Cooling baths of liquid nitrogen, solid carbon dioxide and ethanol, or ice and water are used depending on the melting point of the compound. There is never a temperature difference greater than 120°C between the cooling bath and the calorimeter which makes the control of the system easier.

The vacuum system is shown in Fig. 5. Stainless steel diaphragm valves were chosen because they are more satisfactory than greased valves when hydrocarbons are distilled through the system. A known weight of hydrocarbon can be distilled in vacuum into the calorimeter from a special ampoule shown in Fig. 6. A system is provided for admitting helium to the calorimeter jacket. Because of heat conduction down the filling tube, it is not possible to reach a temperature below —100°C with a liquid nitrogen cooling bath and the jacket evacuated. A small pressure of helium in the jacket promotes cooling of the adiabatic shield and the calorimeter and temperatures down to —170°C can be reached.

2. *The electrical energy circuit*

The circuit is based on the design of WESTRUM AND ROBINSON[11] and the principle is shown in Fig. 7. The calorimeter and dummy heater are of the same resistance so

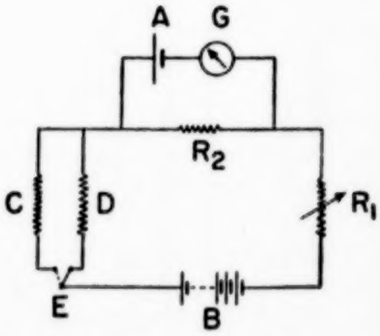

Fig. 7. Simplified electrical energy circuit.

A	standard cell
B	lead storage cells
C	calorimeter heater
D	dummy heater
E	SPDT switch
G	galvanometer
R_1	variable resistance
R_2	fixed resistance

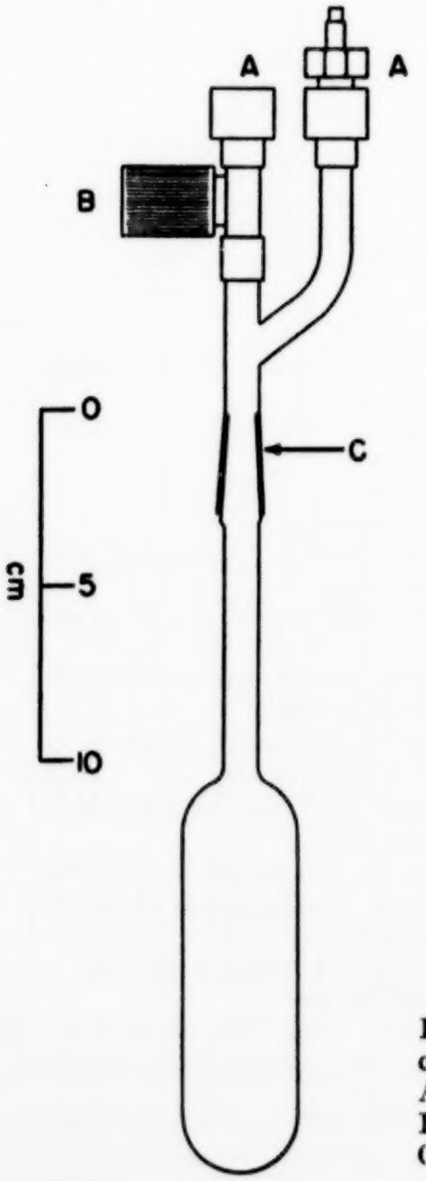

Fig. 6. Ampoule for weighing hydrocarbon before distilling into calorimeter.

A	metal-metal vacuum couplings (Hoke)
B	bellows valve with Kel-F gaskets (Hoke)
C	metal-glass soldered joint (standard taper 12-30)

that substitution of one for the other has no effect on the current flowing through the circuit. This current is varied using R_1 until the galvanometer, G, shows zero deflection. The voltage drop across R_2 is then that of the standard cell and the current through the heater is equal to this voltage divided by R_2. If the calorimeter heater resistance is H, the energy input for a period of t seconds is i^2Ht joules. The assumption is that the resistances of the calorimeter heater and the balancing resistance (R_2) are not changed by the passage of current and this is entirely reasonable as these resistances are made of manganin wire and the currents used are small.

The complete circuit, shown in Fig. 8, is developed from the simple circuit in the following ways. With switch S_2 it is possible to use 7 different currents by selecting different resistances across which the standard cell is balanced and adjusting the voltage across the circuit provided by the lead storage cells and the total resistance. The characteristics of the seven different rates of heat input are given in Table I. Coarse, medium and fine current controls are provided by the systems S_6, $R_2R_3R_4$ and $R_5R_6R_7$, respectively. The dummy heater is the system $R_{24}R_{25}R_{26}$. The resistance of the dummy heater must be varied to equal that of the calorimeter heater as the

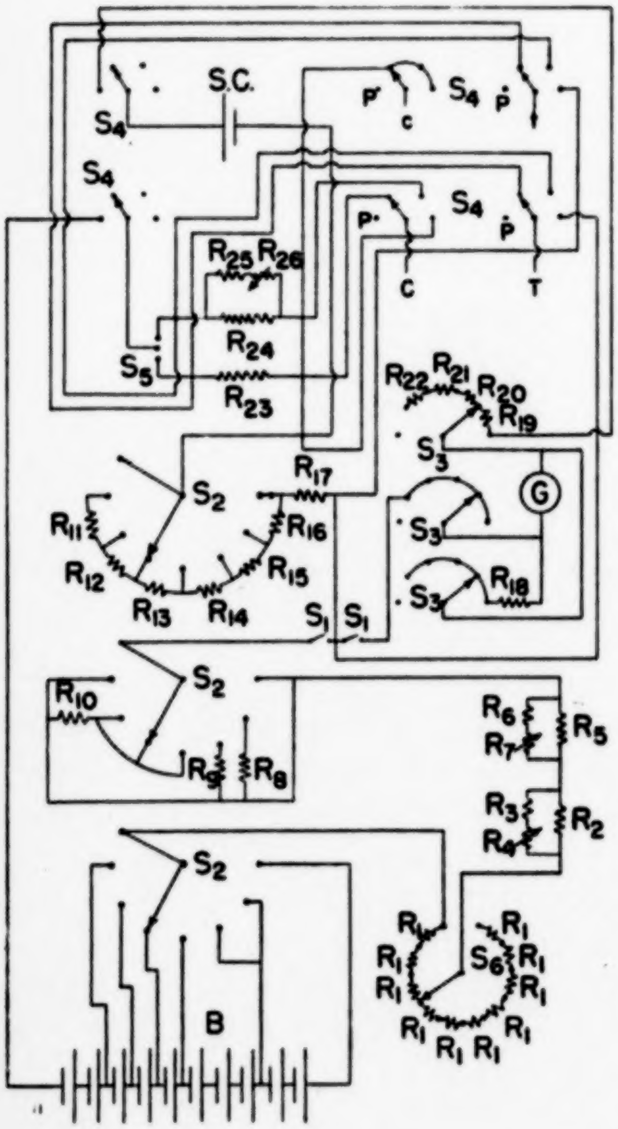

Fig. 8. Circuit for electrical energy inputs.

B	lead storage cells (20 V)
G	"Rubicon" box galvanometer (4.5 mV/mm)
SC	standard cell (Eppley)
S_1	DPST rotary switch
S_2	3P8T rotary switch
S_3	3P6T rotary switch
S_4	6P4T rotary switch
S_5	SPDT relay switch
S_6	SP11T rotary switch
R_1	5 Ω
R_2	15 Ω
R_3	20 Ω
R_4	200 Ω (variable)
R_5	2.5 Ω
R_6	5 Ω
R_7	15 Ω (variable)
R_8	10 Ω
R_9	50 Ω
R_{10}	30 Ω
R_{11}	10.46 Ω
R_{12}	10.40 Ω
R_{13}	5.28 Ω
R_{14}	4.63 Ω
R_{15}	3.95 Ω
R_{16}	1.56 Ω
R_{17}	7.37 Ω
R_{18}	50 Ω
R_{19}	5 KΩ
R_{20}	45 KΩ
R_{21}	0.5 MΩ
R_{22}	5 MΩ
R_{23}	108 Ω calorimeter heater
R_{24}	111.1 Ω
R_{25}	750 Ω dummy heater
R_{26}	250 Ω (variable)
ctCT	connections to Mueller Bridge
p	connections to platinum resistance thermometer

TABLE I

VARIOUS RATES OF HEAT INPUT TO THE CALORIMETER

Position	*Approximate value of balancing resistance (ohms)*	*Approximate value of the current (amperes)*	*Approximate number of calories input in 10 minutes*
1	43.648	0.02334	8.3
2	33.188	0.03070	14.4
3	22.789	0.04471	30.4
4	17.505	0.05820	51.5
5	12.878	0.07911	95.1
6	8.932	0.10888	180.2
7	7.374	0.13816	290.2

latter depends on the temperature. Switch S_4 selects the resistance to be measured with the Mueller Bridge (Leeds and Northrup, Type G2), namely the resistances of the thermometer, calorimeter heater, dummy heater, and current balancing resistance. The galvanometer for current balance is protected by a shunt S_3.

To obtain the total energy input, a known current is passed through the known calorimeter heater resistance for a measured period of time. The timing circuit is shown in Fig. 9. Switch S_3 is automatically closed when the stop watch starting lever is depressed and if S_1 is also closed, current will pass through the relays which then lock into their new positions. In starting the stop watch, current can be thrown from the dummy to the heater and at the end of the period when the watch is stopped, the current is thrown back to the dummy. The time for the heating period can then be read at leisure. Indicator lamps are provided to show through which unit, dummy or heater, the current can be passed.

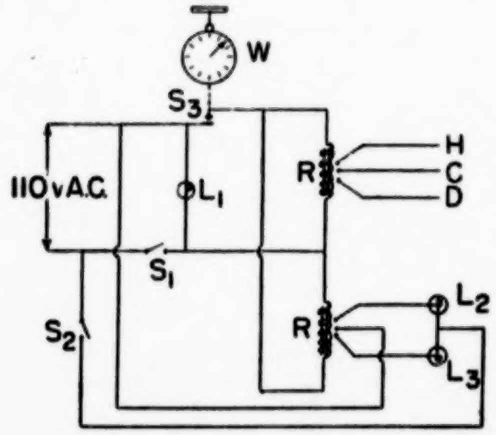

Fig. 9. Timing switch circuit.

W	stopwatch (Clebar to 0.02 second)
S_1	SPST switch to energize relay circuit
S_2	SPST switch for indicator lamps
S_3	Morse key mechanically linked to stopwatch starting lever
R	SPDT locking relays
L_1	indicator lamp for relay circuit
L_2	red indicator lamp
L_3	green indicator lamp
CH	connections to calorimeter heater
CD	connections to dummy heater

When adding energy to the calorimeter, it is necessary to keep only the galvanometer at zero using the current controls, making the process extremely simple. The resistance measurements required are made at other times and the energy input is determined with great precision.

3. *The adiabatic control*

The circuits are shown in Fig. 10. The output of the thermopile results in a deflection of the high sensitivity galvanometer. The adiabatic shield heating current is controlled by a variable transformer and variable resistance. Alternating current is used but because the calorimeter system is grounded the adiabatic shield itself screens the thermopile from any pick-up.

It is not possible to achieve exactly uniform temperatures and adiabatic control is not necessarily maintained at zero EMF of the thermopile. The appropriate deflection of the galvanometer for adiabatic control is obtained for each experiment by finding that deflection which results in a stationary calorimeter temperature, to ± 0.0001°C. After several experiments have been done the approximate positions for adiabatic control are known which makes the finding of the correct position comparatively simple. Adiabatic control is easier when there is helium in the jacket than when the jacket is evacuated, but in the former case closer control is necessary and no great effect on the overall accuracy is found.

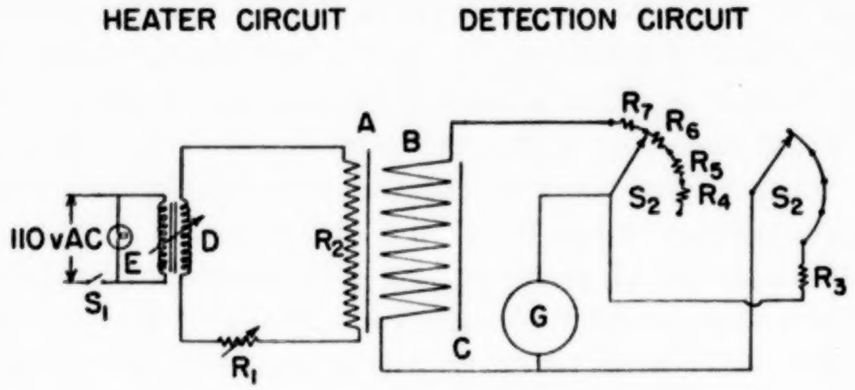

Fig. 10. Circuits for adiabatic control.

A	adiabatic shield surface
B	chromel (28 B and S) — constantan (30 B and S) 30 junction thermopile
C	calorimeter surface
D	variable transformer (Powerstat Type 20)
E	indicator lamp
G	galvanometer (Leeds and Northrup Type HS-2285-b)
S_1	SPST toggle switch
R_1	50 Ω variable resistance
R_2	shield heater (20 Ω)
R_3	50 Ω galvanometer damping resistance
R_4	20 KΩ
R_5	7 KΩ
R_6	2 KΩ
R_7	1 KΩ

Adiabatic control must be maintained throughout the entire experiment but this is done using a single control to vary the adiabatic heating current. This together with the ease of measuring energy inputs makes the operation of the calorimeter extremely simple for a single observer.

V. EXPERIMENTAL PROCEDURE AND CALCULATION OF RESULTS

A measured weight of a low boiling compound can be distilled into the calorimeter from the ampoule shown in Fig. 6. High boiling compounds are syphoned into the calorimeter through a 1/16 inch monel tube from a weighed bottle. Solid compounds must be introduced in the liquid state in the same manner. The hold-up in the syphon is measured separately. High boiling compounds and solids are degassed in the calorimeter.

It is important to have a good crystalline sample of the material in the calorimeter. After crystals have been formed, it is good practice to melt about one half of the material and then allow to cool slowly to remove imperfections in the crystals.

A purity determination is started about 2 or 3°C below the melting point and the balance point for adiabatic control is found then and maintained throughout the entire experiment. The heat capacity of the solid is measured with an energy input causing about a 1°C temperature rise. Then successive energy inputs are made; the steady temperature of the calorimeter being measured after each input. From the approximate heat of fusion of the material in the calorimeter, these energy inputs can be arranged to melt fractions of $^1/_4$, $^1/_3$, $^1/_2$ and almost unity of the material. Sufficient energy is then supplied to melt the remainder of the sample and the heat capacity of the liquid measured with a 1°C temperature rise. The length of time for the experiment depends somewhat on the time for equilibrium temperatures to be reached but on the average takes between 6 and 8 hours.

There is now a succession of energy inputs with associated temperature rises. The heat capacity of the empty calorimeter has been measured from —170°C to +100°C. The mean value for each temperature rise is read from the curve (Fig. 11) and multiplication by the temperature rise gives the energy absorbed by the calorimeter vessel. Subtraction of this from the total gives the energy input to the sample, and also subtraction of the heat capacity of the calorimeter from the total gives that of the sample.

A first approximation to the heat of fusion of the sample is calculated. If the heat capacity of the solid is C_S, the liquid C_L, the temperature for approximately one-half of the material melted is $T_{1/2}$; and E calories are absorbed by the sample in going from T_1 in the solid phase to T_2 in the liquid phase; then the energy of fusion of the material in the calorimeter, D, is given by:

$$D = E - [C_S(T_{1/2} - T_1) + C_L(T_2 - T_{1/2})]$$

At a point in the melting range where the energy input into the sample is E_1 calories measured from the point T_1, the energy absorbed in melting, C_1, up to this point is given to a close approximation by:

$$G = E_1 - C_S\,(T_{1/2} - T_1)$$

Consequently, the reciprocal of the fraction melted ($1/r$) at this point is given by D/G. This reciprocal ($1/r$) is plotted against T to determine the purity of the sample as described above.

Knowing the purity of the sample, the heat capacity of the solid can be corrected for premelting by calculating the number of moles of the major component which are melted during the determination of the heat capacity. With this corrected value for C_S and the value for C_L, both converted into calories/degree C mole, the second cryoscopic constant B can be calculated.

A more precise value for the heat required to fuse the sample is then calculated using the corrected value for C_S, the value for C_L and correcting for the energy quantity which would be absorbed in melting the number of moles of liquid present at the starting temperature T_1. These two corrections to the total energy input to the sample are labelled in the tables as "*∫CpdT*" and "*Premelting*", respectively. From the number of moles in the calorimeter, the heat of fusion per mole is calculated.

VI. THE EXPERIMENTAL RESULTS

All energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833.

The heat capacity of the calorimeter was measured at approximately 10°C intervals between —170°C and +100°C. The temperature rise for each determination was of the order of 1°C. The precision of the measurement was about ±0.3 per cent. The curve of heat capacity against temperature, given as the resistance of the thermometer in ohms, is shown in Fig. 11. The second order transition at about 30°C is due to the Teflon used for insulation in the calorimeter[12]. Its presence is no disadvantage as it is allowed for in measurements in this region.

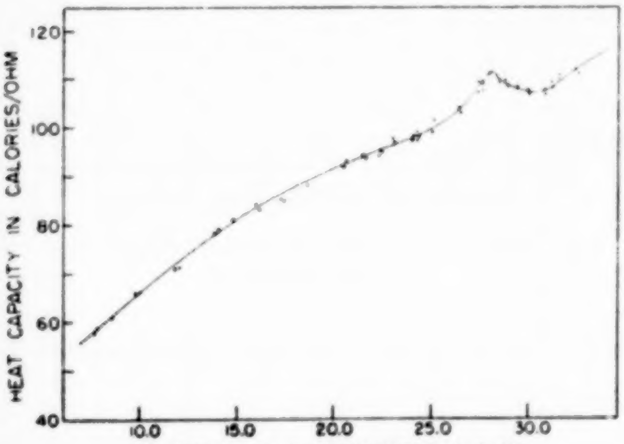

Fig. 11. Heat capacity curve of the empty calorimeter.

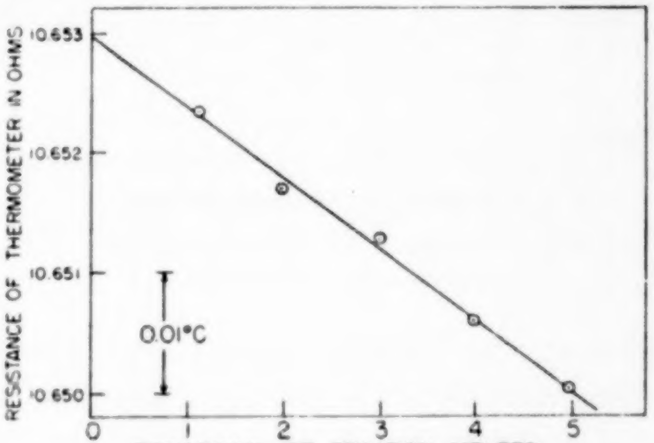

Fig. 12. Curve of fusion data on methylcyclopentane.

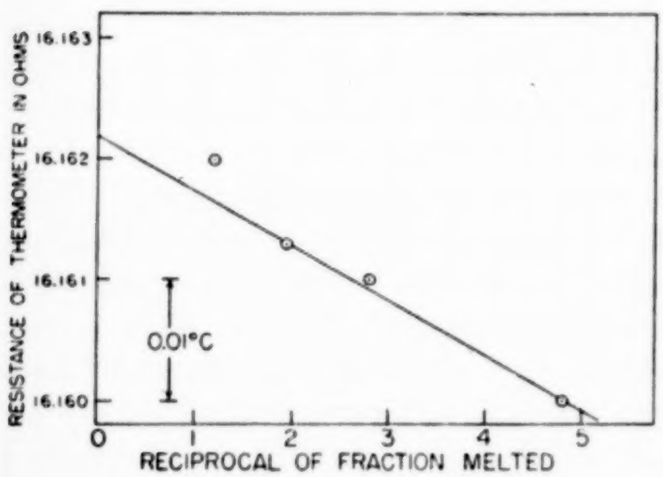

Fig. 13. Curve of fusion data on *n*-heptane.

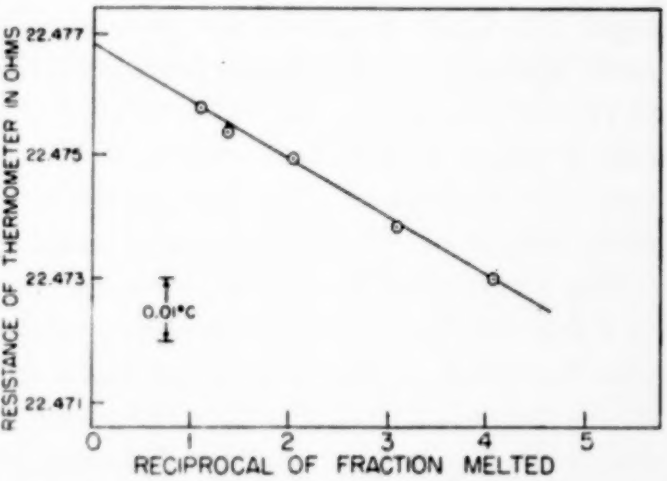

Fig. 14. Curve of fusion data on *n*-decane.

Measurements of the purities and heats of fusion have been made with five API research hydrocarbons, namely, methylcyclopentane (C) (FP —142.455°C), *n*-heptane (B) (FP —90.610°C), *n*-decane (FP —29.661°C), cyclohexylcyclohexane (FP 3.651°C), and *n*-hexadecane (B) (FP 18.165°C). The freezing points given are values in air at 1 atmosphere pressure and are given in references 13 and 14. These compounds were chosen to test the performance of the apparatus over a wide range of temperature. These API research hydrocarbons have been made available by the API Research Project 44 at the Carnegie Institute of Technology. The five compounds were purified from commercially available materials by the API Research Project 6,

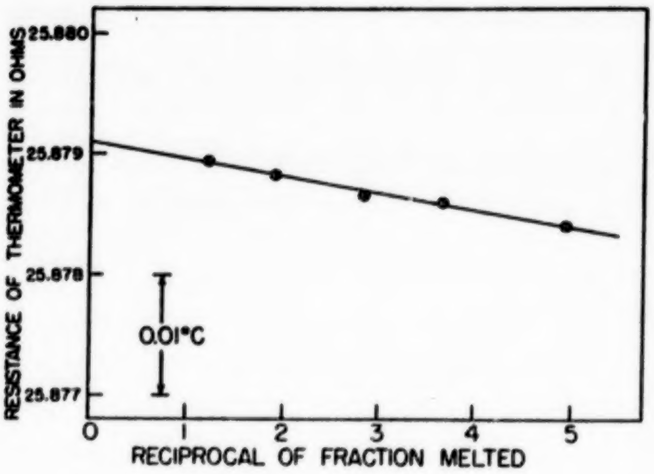

Fig. 15. Curve of fusion data on cyclohexylcyclohexane.

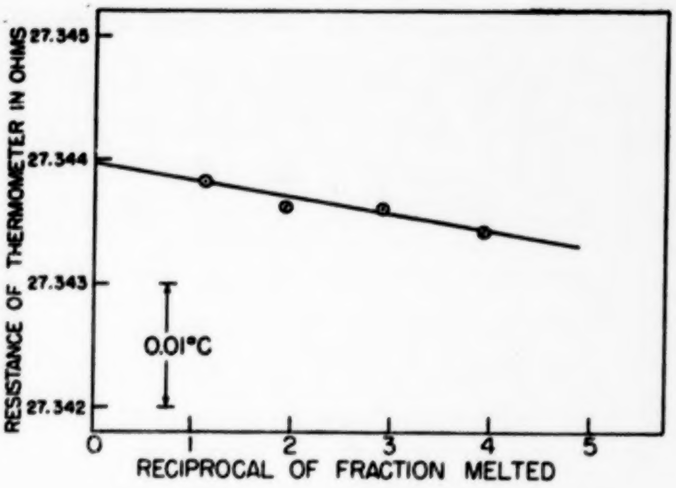

Fig. 16. Curve of fusion data on *n*-hexadecane.

also at the Carnegie Institute of Technology. Description of the purification of these compounds is given in references 14, 19, 20, 21 and 22.

The curves of $(1/r)$ against T for the compounds examined are given in Figures 12, 13, 14, 15, and 16; where T is plotted as the resistance of the platinum thermometer in ohms. The measurements were done under the saturation vapor pressures of the compounds. The experimental data for the purity determinations and for the cryoscopic constants A and B are presented in Table II. The columns headed Cp(solid) and Cp(liquid) are the molar heat capacities of the solid and liquid forms respectively, at the melting point. The value of $(T_1^* - T^s)$ is given for the actual sample measured; and if this is added to the value of T^s separately measured in air by the time-temperature method, T_1^* on that temperature scale can be obtained precisely. Thereafter values of T^s on that same scale provide accurate determinations of purity.

The experimental data for the determination of the heats of fusion are presented in Table III. The errors quoted are merely the deviations from the mean and it is seen that the heat of fusion is determined to about ±0.5 per cent. The heats of fusion were calculated from the data obtained in the purity determination when the sample was melted in stages. Greater accuracy could be obtained by melting the sample in a single stage but the values obtained here are sufficiently accurate for our purposes.

Two first order transitions in cyclohexylcyclohexane were found from earlier work in this laboratory from an examination of the time-temperature curve for total freezing[14]. These transitions were examined in the calorimeter in a similar way to the melting experiments. The transition temperatures were found by plotting temperature against the fraction transposed and the heats of transition were found in a similar way to the heats of fusion. The heat capacities of the various crystalline forms were measured and used in the calculation. The experimental data for these heats of transition are presented in Table IV.

VII. COMPARISON WITH PREVIOUS DATA

This comparison is presented in Table V. Purities have been compared only when the previous determination was made on the same sample as used in this investigation. Methylcyclopentane and *n*-heptane were the first two compounds examined and there is the possibility of slight contamination in these cases.

The agreements found with previous measurements are in general excellent. They

TABLE II

THE CRYOSCOPIC CONSTANTS AND PURITIES OF THE SAMPLES MEASURED

API research sample	*Number of determinations*	*A (mole fraction/°C)*	T_1^* *(°C)*	$T_1^*-T^s$ *(°C)*	*Impurity mole percent*	*(cal/°C mole) Cp(solid)*	*(cal/°C mole) Cp(liquid)*	*B* *(°C⁻¹)*
Methylcyclopentane (C)	3	0.04878	−142.434[a]	0.0060	0.0293 ± 0.0026	18.26	29.99	0.0044
n-Heptane (B)	3	0.05070	−90.590[a]	0.0042	0.0211 ± 0.0018	32.17	47.52	0.0033
n-Decane	2	0.05825	−29.657[a]	0.0096	0.060 ± 0.015	52.39	71.10	0.0028
Cyclohexyl-cyclohexane	1	0.01090	3.707	0.0013	0.0015 ± 0.0002	55.84	63.90	0.0012
n-Hexadecane (B)	1	0.07560	18.175[a]	0.0015	0.012 ± 0.002	93.30	121.11	0.0023

[a] The values of the triple points (T_1^*) for these compounds have been selected from the work of the U. S. Bureau of Mines, Bartlesville, Oklahoma, given in references 15, 17 and 18. The values were assigned to these compounds for the calibration of the platinum resistance thermometer according to the Callendar equation: $R = R_0\,[1 + at + bt^2 + c(t - 100)t^3]$. Then all temperatures given in this report are in °C on the International Scale.

TABLE III

THE HEATS OF FUSION OF THE COMPOUNDS MEASURED

API research sample	*Number of moles*	*Temperature range °C*	*Total energy input cal*	*∫CpdT cal*	*Premelting cal*		*ΔHm cal/mole*
Methylcyclopentane	0.3637	−143.805 to −141.110	626.64	−23.59	2.47		1664.9
	0.3637	−143.112 to −140.966	614.16	−20.57	5.00		1645.8
						Mean	1655 ± 10
n-Heptane	0.2378	− 91.360 to − 88.750	821.71	−25.85	4.37		3365.1
	0.2378	− 91.245 to − 88.429	820.03	−29.54	5.24		3346.2
	0.2378	− 90.916 to − 89.280	806.41	−17.35	6.56		3345.8
						Mean	3352 ± 10
n-Decane	0.1947	− 30.526 to − 26.145	1378.05	−57.05	15.79		6863.4
	0.1947	− 31.301 to − 28.096	1370.96	−38.45	8.06		6885.3
						Mean	6874 ± 12
Cyclohexylcyclohexane	0.1861	2.238 to 4.616	331.69	−26.11	0.27		1643.5
	0.1861	2.959 to 4.854	326.76	−21.44	0.44		1643.0
						Mean	1643.2 ± 0.5
n-Hexadecane	0.09548	16.935 to 20.113	1236.40	−33.48	1.63		12615.7
	0.09548	15.885 to 19.288	1256.98	−32.14	1.43		12843.2
						Mean	12730 ± 100

TABLE IV

THE HEATS OF TRANSITION OF CYCLOHEXYLCYCLOHEXANE

Transition	*Temperature of transition °C*	*Number of moles*	*Temperature range °C*	*Total energy input cal*	*$\int C_p dT$ cal*	*ΔH(transition) cal/mole*
Upper	—0.14 ± 0.03	0.1861	—0.642 to 1.193	385.68	—20.52	1962 ± 15
Lower	—5.70 ± 0.05	0.1861	—7.236 to —3.489	211.20	—32.63	960 ± 12

TABLE V

COMPARISON WITH PREVIOUS DATA

API research sample		*ΔH_m cal/mole*	*B °C⁻¹*	*Impurity mole percent*	*cal/°C mole*	
					Cp(solid)	*Cp(liquid)*
Methylcyclopentane (C)	This work	1655 ± 10	0.0044	0.0293 ± 0.0026	18.26	29.99
	Previous work[15]	1656 ± 4	0.0046	0.01 ± 0.01[14]	19.51	29.89
n-Heptane (B)	This work	3352 ± 10	0.0033	0.0211 ± 0.0018	32.17	47.52
	Previous work[16]	3351.5 ± 2	0.0033	0.004[17]	32.51	48.41
n-Decane	This work	6874 ± 12	0.0028	0.060 ± 0.015	52.39	71.10
	Previous work[18]	6863 ± 2	0.0030	0.089 ± 0.04	55.32	71.00
Cyclohexylcyclohexane	This work	1643.2 ± 0.5	0.0012	0.0015 ± 0.0002	55.84	63.90
	Previous work[14]	1661 ± 20		0.016 ± 0.008		
n-Hexadecane (B)	This work	12730 ± 100	0.0023	0.012 ± 0.002	93.30	121.11
	Previous work[18]	12753 ± 3	0.0027	0.02 ± 0.02[14]	95.20	120.08

are poorest for the heat capacity of the solid at the melting point but in this region the values are made less certain because of premelting.

The precision with which purity can be determined depends directly upon the precision of measurement of the difference between the freezing point of the actual sample and that for zero impurity. For very highly purified samples this difference can be determined with this apparatus to within a few ten-thousandths of a degree C; *cf.* Table II, cyclohexylcyclohexane and *n*-hexadecane. This precision of measurement has been obtained with this apparatus combined with great simplicity of operation.

ACKNOWLEDGEMENTS

The author wishes to thank A. J. Streiff for his constant interest and helpful discussions contributing to this work. The author also wishes to thank Professor F. D. Rossini for his suggestion of the problem and for his advice and encouragement.

SUMMARY

A calorimetric apparatus has been constructed for the determination of the mole fraction of impurity in a highly purified sample of a chemical compound by measurement of the temperature of solid-liquid equilibrium as a function of the fraction of the sample melted. An experimental value of the heat of fusion of the compound is also obtained, thus yielding the cryoscopic constant A. The apparatus, though relatively simple to operate, has given results of good precision. The method has been tested over a wide temperature range using methylcyclopentane, *n*-heptane, *n*-decane, cyclohexylcyclohexane, and *n*-hexadecane, which have freezing points ranging from —142°C to +18°C.

RÉSUMÉ

Un appareil calorimétrique a été construit pour la détermination de la fraction molaire d'impureté d'un échantillon hautement purifié d'un composé chimique par la mesure de la température d'équilibre solide-liquide en fonction de la fraction fondue de l'échantillon. Une valeur expérimentale de la chaleur de fusion est également obtenue donnant ainsi la constante cryoscopique A. Quoiqu'il soit relativement facile à manier, cet appareil a donné des résultats d'une bonne précision. La méthode a été contrôlée dans un grand domaine de température en employant le méthylcyclopentane, le *n*-heptane, le *n*-décane, le cyclohexylcyclohexane et le *n*-hexadécane qui ont des points de congélation situés entre —142°C et 18°C.

ZUSAMMENFASSUNG

Es wurde ein kalorimetrischer Apparat konstruiert, der zur Bestimmung der Molfraktion an Verunreinigung in einer weitgehend gereinigten Probe einer chemischen Verbindung durch Messung der Fest-Flüssigkeit-Gleichgewichts-Temperatur als Funktion des geschmolzenen Teiles der Probe dient. Ein experimenteller Wert der Schmelzwärme wird ebenfalls erhalten und dadurch auch die kryoskopische Konstante A. Obwohl der Apparat relativ einfach zu bedienen ist, gibt er doch genaue Resultate. Die Methode wurde in einem weiten Temperaturbereich geprüft, und zwar unter Verwendung von Methylcyclopentan, *n*-Heptan, *n*-Dekan, Cyclohexylcyclohexan und *n*-Hexadekan deren Gefrierpunkte zwischen —142°C und 18°C liegen.

REFERENCES

[1] B. J. Mair, A. R. Glasgow, Jr. and F. D. Rossini, *J. Research Natl. Bur. Standards*, 26 (1941) 591.
[2] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, 35 (1945) 355.
[3] W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, 32 (1944) 197.
[4] F. W. Schwab and E. Wichers, *Temperature - Its Measurement and Control in Science and Industry*, pp. 256-264, Reinhold Publishing Corp., New York, 1941.
[5] F. D. Rossini, *Chemical Thermodynamics*, John Wiley and Sons, New York, 1950.
[6] S. V. R. Mastrangelo and R. W. Dornte, *J. Am. Chem. Soc.*, 77 (1955) 6200.
[7] H. L. Johnston and W. F. Giauque, *J. Am. Chem. Soc.*, 51 (1929) 3194.
[8] J. G. Aston, H. L. Fink, J. W. Tooke and M. R. Cines, *Anal. Chem.*, 19 (1947) 218.
[9] D. D. Tunnicliff and H. Stone, *Anal. Chem.*, 27 (1955) 73.
[10] J. T. Clarke, H. L. Johnston and W. de Sorbo, *Anal. Chem.*, 25 (1953) 1156.
[11] E. F. Westrum, Jr. and H. P. Robinson, *The Transuranium Elements*, National Nuclear Energy Series IV, 14B, p. 889, McGraw-Hill Book Company, Inc., New York, 1949.

[12] G. T. FURUKAWA, R. E. MCCOSKEY AND G. J. KING, *J. Research Natl. Bur. Standards*, 49 (1952) 273.

[13] American Petroleum Institute Research Project 44, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

[14] American Petroleum Institute Research Project 6, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania. Unpublished data.

[15] D. R. DOUSLIN AND H. M. HUFFMAN, *J. Am. Chem. Soc.*, 68 (1946) 173.

[16] T. B. DOUGLAS, G. T. FURUKAWA, R. E. MCCOSKEY AND A. F. BALL, *J. Research Natl. Bur. Standards*, 53 (1954) 139.

[17] G. WADDINGTON. U. S. Bureau of Mines, Bartlesville, Oklahoma (Private communication to F. D. ROSSINI).

[18] H. L. FINKE, M. E. GROSS, G. WADDINGTON AND H. M. HUFFMAN, *J. Am. Chem. Soc.*, 76 (1954) 333.

[19] A. R. GLASGOW, JR., E. T. MURPHY, C. B. WILLINGHAM AND F. D. ROSSINI, *J. Research Natl. Bur. Standards*, 37 (1946) 141.

[20] A. J. STREIFF, E. T. MURPHY, J. C. ZIMMERMAN, L. F. SOULE, V. A. SEDLAK, C. B. WILLINGHAM AND F. D. ROSSINI, *J. Research Natl. Bur. Standards*, 39 (1947) 321.

[21] A. J. STREIFF, A. R. HULME, P. A. COWIE, N. C. KROUSKOP AND F. D. ROSSINI, *Anal. Chem.*, 27 (1955) 611.

[22] A. J. STREIFF, L. H. SCHULTZ, A. R. HULME, J. R. TUCKER, N. C. KROUSKOP AND F. D. ROSSINI, *Anal. Chem.*, 29 (1957) 361.

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AN AUTOMATIC (OR SEMI-AUTOMATIC) APPARATUS FOR THE DETERMINATION OF MELTING CURVES

by

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INTRODUCTION

The apparatus to be described is a "thin film" apparatus operating automatically within a range of about 0.2°C and a temperature sensitivity of about 0.001°C. Larger temperature ranges may be investigated, either fully automatically with a temperature sensitivity which is inversely proportional to the temperature range to be investigated, or semi-automatically by dividing the temperature range into parts of about 0.2°C. In the latter case the temperature sensitivity remains 0.001°C.

The calorimetric part of the apparatus is essentially the same as that of the hand-operated apparatus, mentioned in previous papers[1]. Since up to now we have not given any account of the principles on which the "calorimeter" is based, it seemed useful to begin by doing so and then to describe an adapted system of controlling and recording.

Principle of the apparatus

The "calorimeter" consists of a cylindrical metal block containing a coaxial cylindrical air space. The substance to be investigated is contained in an annular space between the "thermometer" and the inside wall of the measuring vessel. The axis of the measuring vessel coincides with the axis of the block.

The metal block is heated at such a rate that its temperature differs constantly, by a distinct number of degrees, from the temperature indicated by the central thermometer. Consequently the flow of heat from the wall of the block to the measuring vessel (or reverse) is almost constant.

This method as such for obtaining a constant heat supply has already been applied by THOMAS AND PARKS[2].

In the apparatus described here the substance is spread in a single thin layer and no stirring is applied. In the hand-operated apparatus the temperatures of the block and the measuring vessel are indicated by mercury thermometers. (A special type of *small* Beckmann thermometer, subdivided in 0.05°C, rendered good service.)

In the automatic apparatus resistance thermometers have been applied. The resistance of the inner thermometer is recorded as a function of time, whereas the controller for heating the block operates on the difference of the specific resistance of the outer and inner thermometer.

THE CALORIMETER

Description of the calorimeter

The calorimeter (see Fig. 1) consists of an aluminium cylindrical block (5) with a central bore, closed by a forced-in aluminium cover. A hole in this cover permits introduction of the glass measuring vessel (6). When in use the measuring vessel contains a (central) thermometer. A second (outer) thermometer may be inserted in a thermometer well (8). The block (5) is surrounded by a heating element (4) (400 ohms); this consists of a heating coil of constantan strip insulated by glass wool .The coil is enclosed between two single layers of thin asbestos paper. The block, together with the heating element, is contained in a closely fitting cylindrical aluminium jacket (3). It is suspended to the large asbestos cement cover (7) by means of thin stainless steel rods. The cover (7) rests on the outer jacket (1) containing the Dewar flask (2).

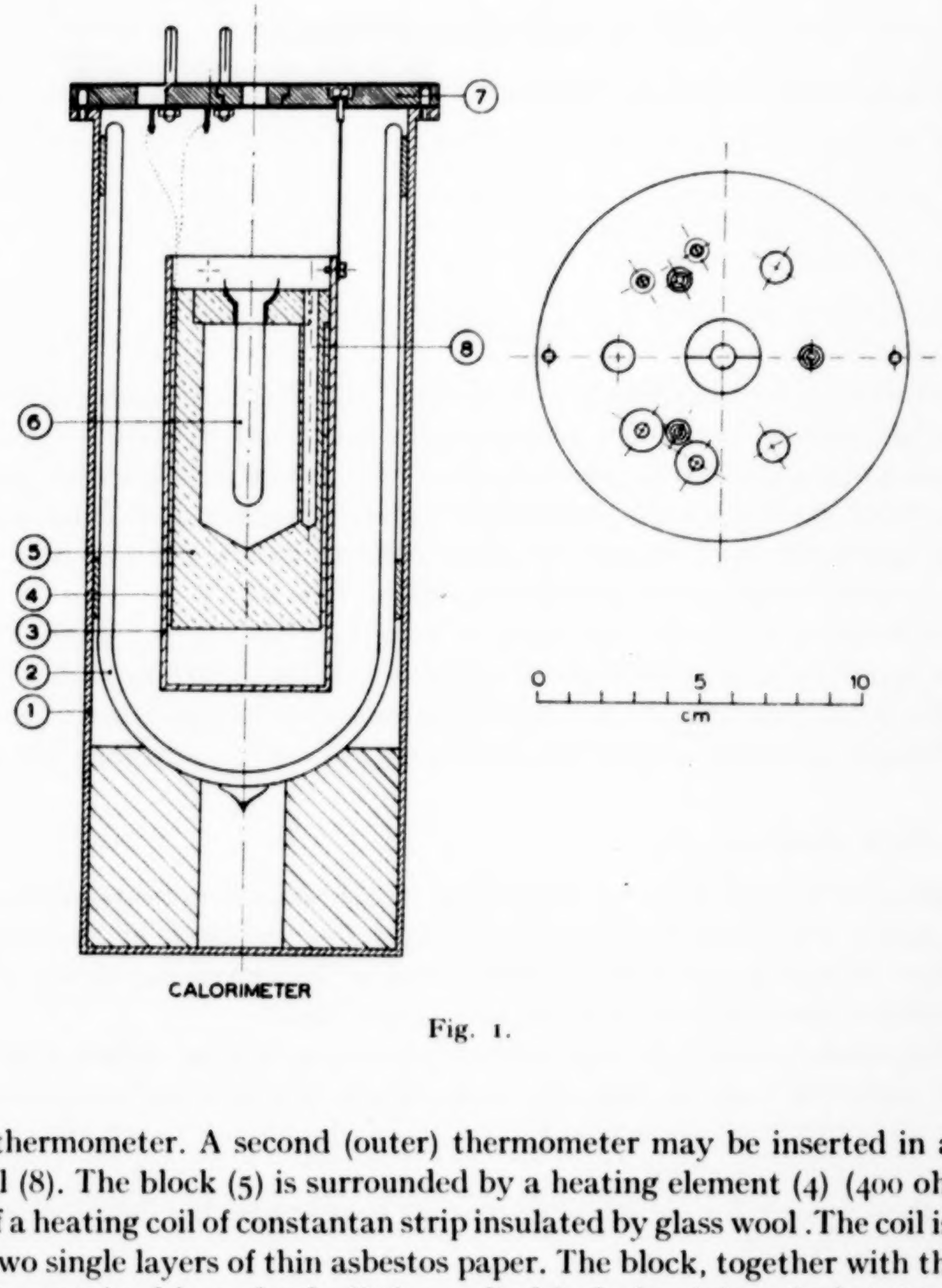

Fig. 1.

Dimensions of the measuring vessel

The considerations on which the dimensions of the measuring vessel, the layer of substance, and the thermometer, were based are given in the accompanying paper[3].

Dimensions of the block

The outer dimensions of the measuring vessel having been decided on, the optimal dimensions of the block were estimated on the basis of the following considerations.

As is obvious, the heat supplied to the measuring vessel increases when the temperature difference between the block and the measuring vessel is increased. In order to obtain a reliable heating curve the heat supply, and thus the temperature difference, should be low. On the other hand, a low temperature difference involves great demands on the sensitivity of the system controlling this temperature difference. The accuracy aimed at, combined with the sensitivity of the controlling system set a lower limit for the allowable temperature difference. Therefore, it is worthwhile to investigate at what dimensions of the metal block the heat supply to the measuring vessel is minimal at a given temperature difference.

Heat is transferred from the inside wall of the block to the measuring vessel by means of conduction and radiation. (Since the temperature differences occurring are relatively small, convection is neglected.)

As the length of the cylindrical bodies amounts to several times their respective diameters it is permissible to estimate the heat transfer to the measuring vessel by applying the laws obtaining to coaxial cylindrical bodies of infinite length.

The heat (Q) transferred per unit time and per unit length to the inner cylinder of a system of two coaxial cylinders separated by an annular air space amounts to:

$$Q = \frac{2\pi\lambda(T_2 - T_1)}{\ln r_2/r_1} + 2\pi r_1 \left[\left(\frac{T_2}{100}\right)^4 - \left(\frac{T_1}{100}\right)^4\right] C \text{ cal/sec.cm}^{*} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where the first term of the right-hand member represents the heat transferred by conduction and the second term represents the contribution of radiation, and

$$\frac{1}{C} = \frac{1}{C_1} + \frac{r_1}{r_2}\left(\frac{1}{C_2} - \frac{1}{C_s}\right)$$

Further: λ is the heat conductivity of air
r_1 is the outer radius of the inner cylinder (measuring vessel)
r_2 is the inner radius of the outer cylinder (metal block)
T_1 absolute temperature at r_1
T_2 absolute temperature at r_2
C_s is the black body emissivity
C_1 is the emissivity of the surface of the inner cylinder
C_2 is the emissivity of the inner surface of the outer cylinder.

Discussion of equation (1)

As is clear from equation (1), the heat transferred to the measuring vessel depends on quite a number of factors, *viz.*, C_1, C_2, λ, r_1, r_2, T_1 and T_2.

C_1 represents the emissivity of the outer wall of the measuring vessel. A glass measuring vessel is easy to make and permits inspection of the sample. The high emissivity of glass is a drawback that may be compensated to a large extent when the emissivity of the block (C_2) is low. It was therefore decided to choose a glass measuring vessel, thus fixing the value of C_1 at 0.94 C_s, which is the value obtaining for glass.

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* See *e.g.* A. SCHACK, *Der Industrielle Wärmeübergang*, Düsseldorf, 1953.
W. H. MC ADAMS, *Heat Transmission*, New York, 1942.

The influence of the remaining factors is illustrated by a series of graphs (see Figs. 2, 3, 4, 5).

Fig. 2 shows the flow of heat (Q) as a function of r_2 at different values of C_2. (r_1 = 0.4 cm; $T_1 = 573°C$; $T_2 = 574°C$; and $\lambda = 10^{-4}$ cal/cm.sec degree.) It appears that a low value of C_2 is preferable.

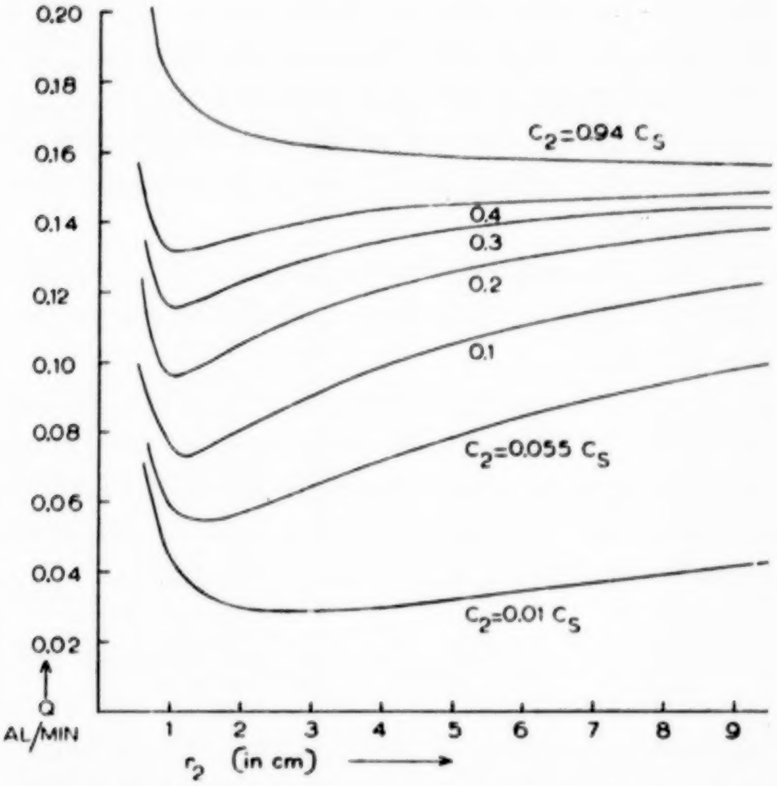

Fig. 2. Flow of heat as function of inner radius of calorimeter at different emissivities.

Polished surfaces of several metals have a low emissivity. However, the emissivity of these surfaces soon increases when exposed to the atmosphere of a laboratory at elevated temperatures, with the exception of surfaces of gold or non-polished aluminium. Non-polished aluminium has a fairly low emissivity, *viz.* $C_2 = 0.055\ C_s$. Further, aluminium has a high temperature conductivity and is inexpensive. Accordingly, the block was made of aluminium, thus fixing the value of C_2 at about 0.055 C_s. The curve of Fig. 2 obtaining for $C_2 = 0.055\ C_s$ shows a minimum at $r_2 = 1.5$ cm.

Fig. 3 shows the flow of heat (Q) as a function of r_2 at different temperatures. The curves of this graph hold good for $C_1 = 0.94\ C_s$; $C_2 = 0.055\ C_s$; $r_1 = 0.4$ cm and $T_2 - T_1$ = 1°C; λ is a temperature function varying from $0.5 \cdot 10^{-4}$ at 273°K to 10^{-4} cal/cm.sec degree at 573°K. (The applicable values of λ have been derived from Landolt-Börnstein, Physikalisch-Chemische Tabelle.)

All the curves of Fig. 3 show a minimum. The minima have been connected by a dotted line. It appears that the minima at low temperatures are far less pronounced than those at high temperatures. The value of Q at $r_2 = 1.5$ cm differs only slightly from the minimal value obtainable at a certain temperature within the range of 173-573°K. Therefore a value of $r_2 = 1.5$ cm may be preferable. However, it must be remembered that Q is also a function of r_1 (see Fig. 5).

Fig. 4 shows Q as a function of r_2 at different values of $T_2 - T_1$. ($C_2 = 0.055\ C_s$; r_1 = 0.4 cm; $T_1 = 573°K$; $\lambda = 10^{-4}$ cal/cm. sec degree.) It appears that the minimum in the

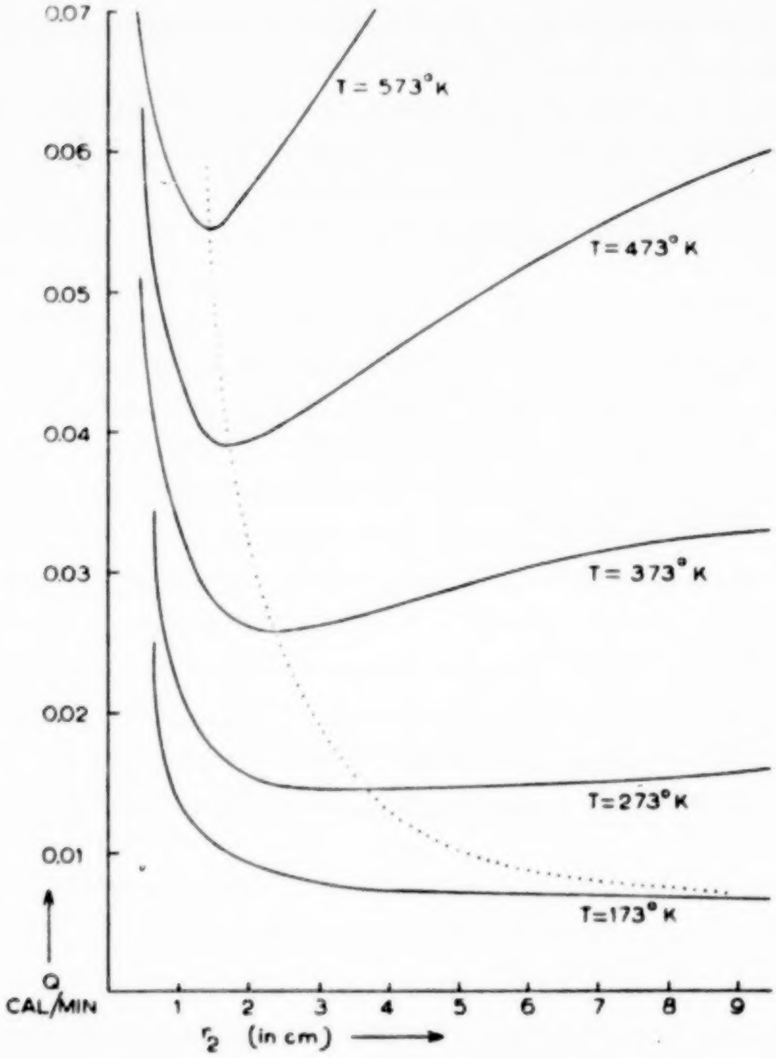

Fig. 3. Flow of heat at different temperature as function of inner radius.

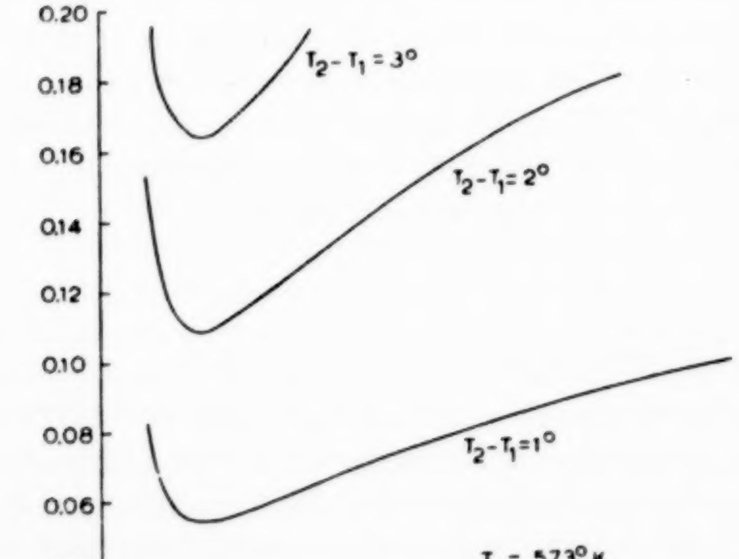

Fig. 4. Flow of heat at different thermal heads as function of inner radius.

(Q, r) curves is independent of $T_2 - T_1$. Further, Q is approximately proportional to $T_2 - T_1$, at least when $(T_2 - T_1) < 3$°C.

Fig. 5 shows Q as a function of r_2 at different values of the outside diameter (r_1) of the measuring vessel. ($C_2 = 0.055\, C_s$; $T_1 = 573$°C; $T_2 = 574$°C; $\lambda = 10^4$ cal/cm. sec degree.)

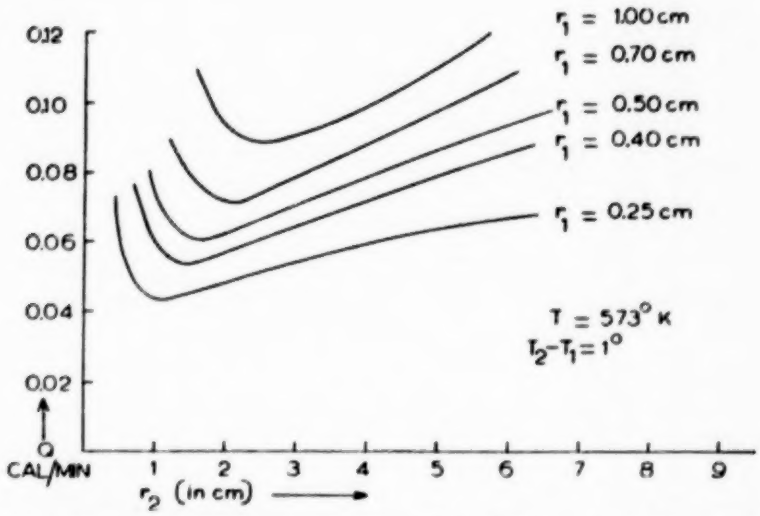

Fig 5. Flow of heat as function of inner radius at different radii of the measuring vessel.

It appears that the minimum in the (Q, r_2) curves shifts to higher values of r_2 when r_1 increases. Therefore the inner radius of the block should be adapted to the outer radius of the measuring vessel. In its turn the outer radius of the measuring vessel depends on the radius of the thermometer (see preceding paper). The radii of suitable mercury thermometers vary from about 0.2 to 0.4 cm. (As will be shown, it is possible to construct resistance thermometers with comparable radii.) This range of thermometer radii corresponds to a range of vessel radii from about 0.25 to 0.5 cm. Within this range of vessel radii the value of r_2 at which Q is minimal varies only from 1.3 to 1.7 cm. Therefore an inside radius (r_2) of the block equal to 1.5 cm has been chosen, this being a mean value permitting the use of commercially available thermometers and ensuring a low heat transfer within a very wide range of temperature.

Experimental checks on equation (1)

Experimental checks on equation (1) have been carried out with aluminium blocks having inner radii of 1.0 and 1.5 cm, respectively. Further, all-glass apparatuses ($C_2 = 0.94\, C_s'$) with inside radii r_2 of 0.9, 1.1, 1.5 and 1.8 cm, respectively, have been investigated. The flow of heat (per unit length of the measuring vessel) during each experiment has been determined by measuring the time required to melt a known amount of substance (per unit length) having a known heat of fusion. The experiments have been carried out at $T_1 = 321$°K or 425°K, and values of $T_1 - T_2$ equal to 2.0, 2.2, 2.5 and 3°C have been applied. The difference between the flow of heat actually found in this series of ten experiments never differed in any of the cases more than 10% from the value calculated.

MEASURING AND CONTROLLING PARTS

Temperature detection system

Electrical detection of temperature and temperature differences may be carried out either with thermocouples or with resistance thermometers. In the case to be discussed here the accuracy aimed at is 0.001°C corresponding with an e.m.f. or $5 \cdot 10^{-8}$ V for a copper-constantan couple.

It is very difficult to build a both stable and linear D.C. amplifier with a noise level as low as $5 \cdot 10^{-8}$ V. According to our experience it is possible to build a linear D.C. amplifier stable within 10^{-6} V without using selected amplifier tubes. Accepting the value of 10^{-6} V as a reasonable lower limit involves the use of a 20-fold thermocouple to obtain an accuracy of 0.001°C. A 20-fold thermocouple, however, if applied in our calorimeter, would upset the whole system of heat transfer because of the relatively large heat conductivity of such a thermopile. Other drawbacks of a thermopile are its relatively large volume and the necessity of a reference point constant within 0.001°C.

Resistance thermometers seem to be more suitable. N.T.C. resistors (thermistors) were rejected because of their relatively small temperature range, instability at temperatures above 100°C, and complicated temperature function. The requirements to be met by a resistance thermometer suitable for our purposes are: high temperature coefficient, high resistance and small volume.

It appeared that these requirements could be met with by selfmade resistance thermometers with a resistance wire of tungsten or platinum.

The resistance thermometer

The total resistance required has been calculated in the following way. Suppose the resistance thermometer to be part of a Wheatstone bridge consisting of four almost equal resistors. Then the bridge signal varies with $\frac{1}{4}\alpha V$ volts per degree, when V is the voltage applied to the bridge and α is the temperature coefficient of the resistance thermometer. Because of the accuracy aimed at and the noise level of the amplifier, the variation of the bridge signal should be larger than 10^{-3} volt degree. Since α equals about 0.4% per degree for tungsten or platinum the voltage fed to the bridge should be at least equal to one volt, causing a voltage over the resistance thermometer of about 0.5 volts. Suppose the bridge to be fed with direct current and the resistance of the thermometer to be R ohms. Then the heat developed by the thermometer amounts to $(0.25\ R \times 0.24$ cal/sec. The total heat required for heating the measuring vessel and its contents amounts to about 10^{-3} cal/sec not allowing more then 10% of the total heat required to be developed by the resistance thermometer. A value for R of at least 600 ohms results.

The size of the sensitive part of the resistance thermometer should preferably be comparable with the bulb of a common mercury thermometer.

It appeared that 5-watt glow lamps contained a coil of tungsten wire having a resistance of about 600 ohms at room temperature. The length of the coil is about 9 cm and its diameter is only 0.1 mm. It proved to be possible to mount such a coil in a helix etched in a small glass tube and to seal the whole in a second thin-walled glass tube of a slightly larger diameter. The ends of the tungsten coil were silver-soldered to platinum leads through the outer glass tube. We also constructed platinum resistance thermometers of comparable size and resistance in almost the same way. Platinum wire of a diameter of 0.015 mm was used. It was wound bifilarly around a glass tube having an etched helix of about three turns per mm. The temperature-sensitive part of these thermometers has a diameter of about 6.5 mm and a length of about 25 mm. The resistance at room temperature is about 600 ohms.

Circuits for measuring and controlling

The circuits for measuring and controlling start with two combined Wheatstone bridges shown in Fig. 6. The measuring bridge (bridge I) consists of two resistance boxes (R_1 and R_2, both 10 × 100 ohm), a five-decades resistance box (R_3) and the measuring thermometer R_m. The controlling bridge (bridge II) contains the box (R_1), the measuring thermometer, the controlling thermometer and a five-decades resistance box (R_4). Both bridges are fed from the same lead accumulator via a Poggendorf circuit (resistance 20 ohms) permitting the application of the following voltages to the bridge: 2, 1, and 0.7 V.

The two bridge signals are fed either to two totally separated amplifiers or to a motor-driven switch which connects alternatively the first or the second bridge to one and the same amplifier. When only one amplifier is used the output of the amplifier is also fed to a switch operating in phase with the input switch. Dead periods are included so as to prevent measuring signals from interfering with controlling signals or reverse. The switches operate at three complete cycles per second.

Both methods of amplification (one or two amplifiers) have been used. Amplification with two separate amplifiers showed to be somewhat advantageous.

The amplified measuring signal is fed to a commercial recorder. Since the output signal amounts to about 2 watt/degree, even recorders without amplification system may be adapted to the amplifier.

The amplified controlling signal (d.c.) is fed to the primary winding of a transformer. The secondary winding of this transformer is inserted in the circuit containing the heating element of the block. Consequently, when the controlling signal (d.c.) increases, the impedance in the circuit of the heating current (a.c.) decreases, thus causing an increase of the heating current. Reversely, a decrease of the controlling signal causes a decrease of the heating current, thus yielding a nice system of proportional control.

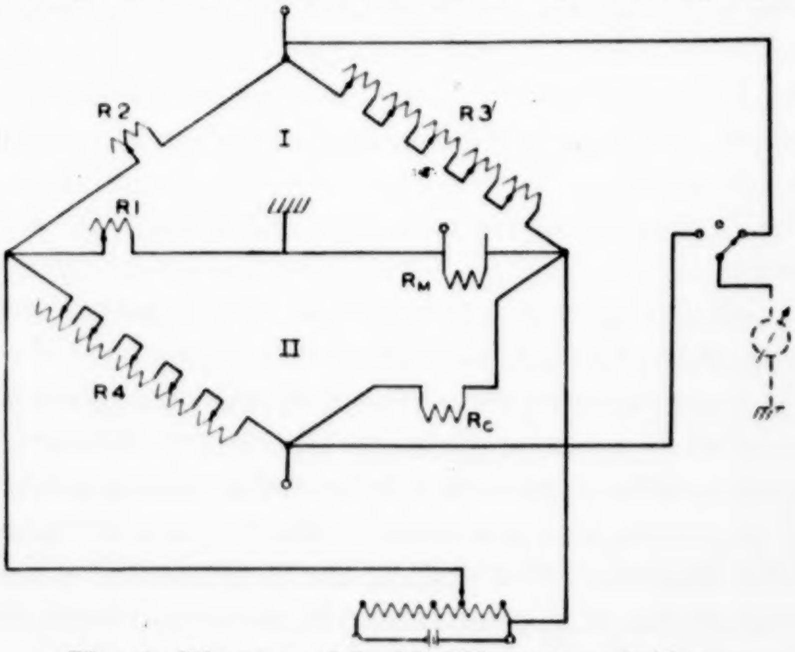

Fig. 6. Diagram of double Wheatstone bridge.

The amplifier(s)

The d.c. signal coming from one of the bridges is fed to a chopper in order to convert d.c. into a.c. After amplification the a.c. signal is again converted into a d.c. signal by a second chopper operating at the same frequency. The choppers are driven by the same synchronous motor. The frequency of the choppers is 40 hertz.

The scheme of a double-purpose (switch-operated) amplifier is shown in Fig. 7.

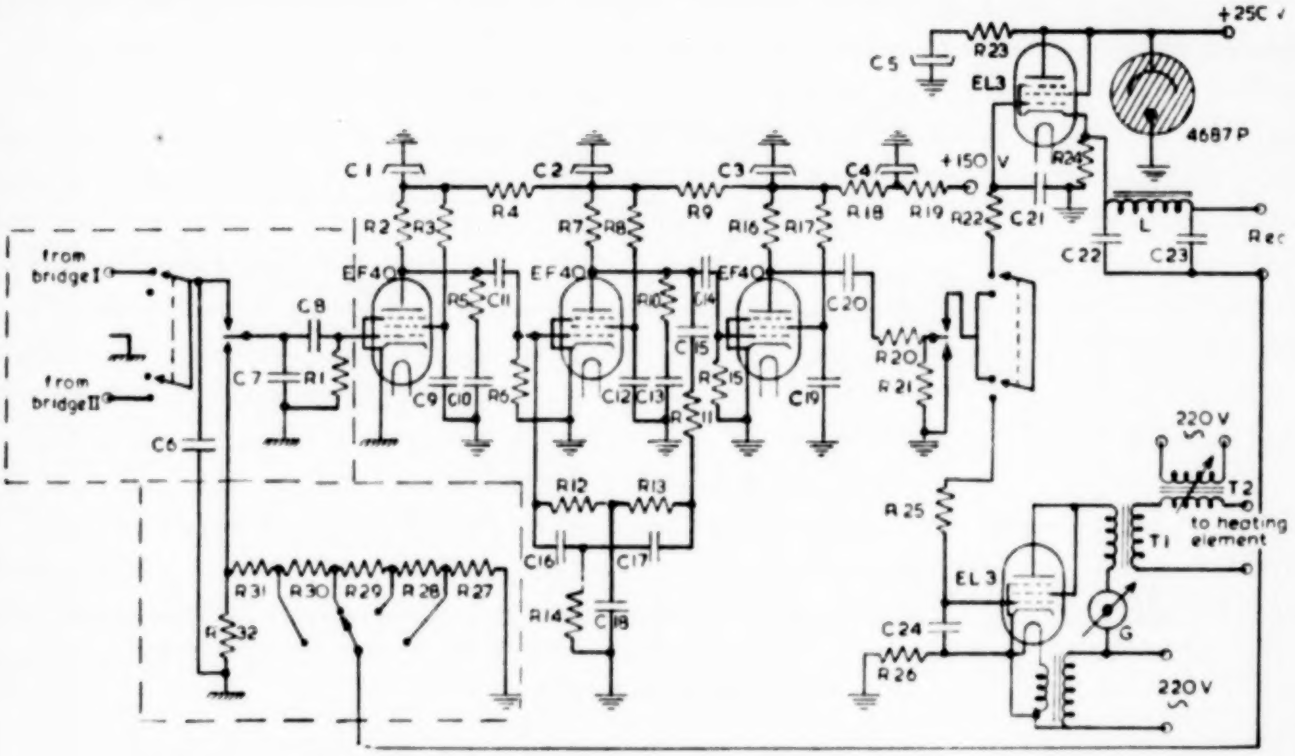
+250 V
R23
C5
EL3
4687 P
C1
C2
C3
C4
+150 V
R24
R4
R9
R18
R19
R22
C21
R2
R3
R7
R8
R16
R17
L
Rec
C22
C23
from bridge I
from bridge II
EF40
EF40
EF40
C8
R5
C11
R10
C14
C20
C7
R1
C15
R15
R20
R21
C9
C10
R6
C12
C13
R11
C19
C6
220 V
T2
to heating element
T1
R12
R13
R25
C16
C17
R31
R30
R29
R28
R27
R14
C18
EL3
C24
R32
G
R26
220 V

Fig. 7. Scheme of microvolt amplifier, controlling and recording system.

TABLE I

RESISTANCES AND CAPACITIES OBTAINING TO FIG. 7

R 1	10 MΩ	R 12	145 KΩ	R 23	8 KΩ
R 2	1.5 MΩ	R 13	145 KΩ	R 24	3.3 KΩ
R 3	6.6 MΩ	R 14	47 Ω	R 25	470 KΩ
R 4	15 KΩ	R 15	10 MΩ	R 26	100 KΩ
R 5	220 KΩ	R 16	330 KΩ	R 27	1 Ω
R 6	10 MΩ	R 17	1.5 MΩ	R 28	4 Ω
R 7	1.5 MΩ	R 18	15 KΩ	R 29	5 Ω
R 8	6.6 MΩ	R 19	10 KΩ	R 30	90 Ω
R 9	15 KΩ	R 20	1 MΩ	R 31	400 Ω
R 10	220 KΩ	R 21	1 MΩ	R 32	1 Ω
R 11	330 KΩ	R 22	3 MΩ		Ω
C 1	8 μF	C 13	100 pF	L 10	henry
C 2	8 μF	C 14	0.025 μF	150	ohm
C 3	8 μF	C 15	5000 pF	G	mA meter
C 4	8 μF	C 16	26500 pF	⏚	separate
C 5	8 μF	C 17	26500 pF		earthing
C 6	4 μF	C 18	53500 pF	⏚	general
C 7	0.01 μF	C 19	0.1 μF		earthing
C 8	0.025 μF	C 20	0.25 μF		
C 9	0.1 μF	C 21	0.1 μF	Rec	recording
C 10	100 pF	C 22	16 μF		mA meter
C 11	0.025 μF	C 23	16 μF		10 mA, 400
C 12	0.1 μF	C 24	0.1 μF		ohm

Since voltages as low as 10^{-6} are amplified, special attention has to be paid to shielding and earthing. The parts to be shielded have been enclosed in broken lines in the diagram. Two different symbols for earthing have been used indicating two separated earthing circuits. When no separate earthing is applied serious difficulties arise.

The choppers

The choppers (see Fig. 8) used, are not unlike the one described by LISTON, QUINN, SARGEANT AND SCOTT[4].

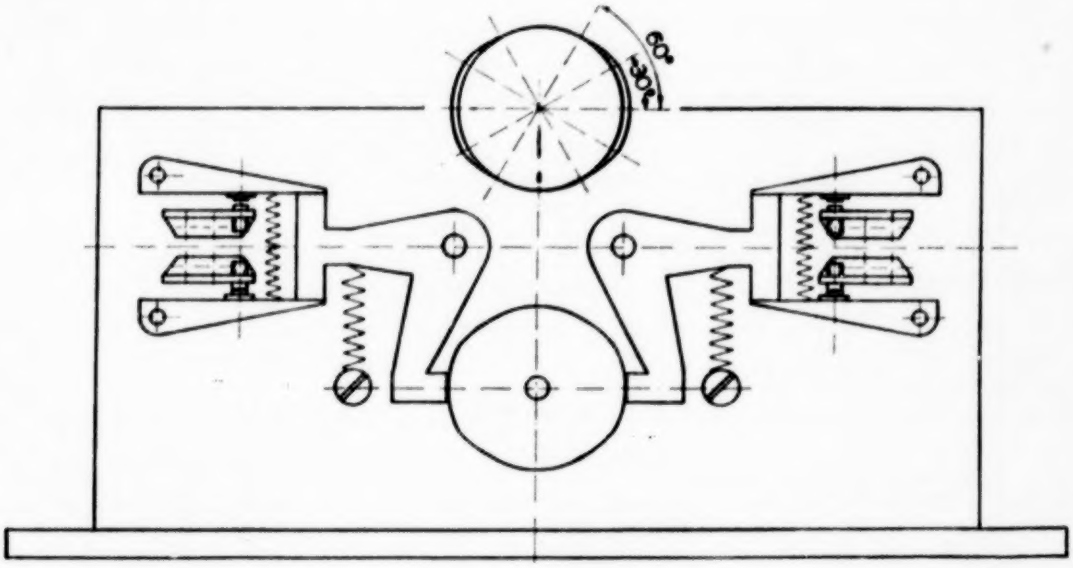

Fig. 8. Chopper.

The contacts are lifted by means of rotating discs driven by one and the same synchronous motor. The disc has a special shape (see insertion in Fig. 8) in order to obtain a high speed of opening and closing of the contacts without causing large displacements of the contacts. This way of opening and closing contacts may have advantages over the method used by LISTON and coworkers; it reduces heat development and possible chattering.

Experimental details

The determination of a heating curve is carried out in the following way. The measuring vessel is filled with a weighed amount of substance. Usually quantities less than 500 mg are sufficient. The measuring thermometer is inserted into the measuring vessel containing the molten substance.

Care is taken that the sensitive part of the thermometer is at equal distance from the bottom and the inner wall of the measuring vessel. The level of the molten substance has to be about 2 mm above the top of the sensitive part of the thermometer. Eventually trapped air-bubbles are removed by gentle tapping. Then the substance is allowed to solidify and the measuring vessel with the thermometer is inserted in the block. The block is heated by switching the feeding transformer of the heating current to full.

The Wheatstone bridge contains a switch which connects the output of the bridge either to the input of the amplifier or to a mV-meter. By equilibrating the bridge on the mV-meter the temperature of the measuring vessel may be followed with an accuracy of about 1°.

When the measuring vessel has attained a desired temperature the heating is switched off and the block is allowed to equilibrate. The variable resistance of the controlling bridge is set on

$$R_4 = R_1 + R_c^\circ\, a\, (T_2 - T_1)$$

where R_c° is the resistance of the controlling thermometer at zero degrees centigrade and $(T_2 - T_1)$ is the temperature difference to be maintained between the block and the measuring vessel*.

As a rule $(T_2 - T_1)$ is about 1.5°C, causing a rate of heating of about 0.3°C per minute.

The variable transformer feeding the heating element is adjusted to such a voltage that it can heat the block at a rate somewhat higher than desired. Provided the voltage is high enough, the setting of the variable transformer is not very critical since the controlling system may reduce the heating current by about 30% when the temperature of the block is only 0.03° high.

The amplifier(s) and the recorder are started and the apparatus records the heating curve. The sensitivity of the aparatus may be varied by means of a switch changing the back feed of the amplifier.

When the recorder shows full deflection, R_3 is increased by a distinct amount, *and the recording pen returns to near zero deflection.*

The number of times R_3 has to be increased during a determination depends on the temperature range to be investigated and the sensitivity switched on. The sensitivity may be set so that a full scale deflection (10 cm) of the recorder corresponds with 0.12, 0.25, 0.40 or 3.5°C.

The apparatus shows a rapid response. When the voltage of the heating current is suddenly changed by about 25% the heating current is fully readjusted within 45 seconds. When the resistance R_3 is changed so that the recording pen travels over the full scale it attains its new final position within 40 seconds, whereas over 95% of the scale is travelled by the pen within one second.

The experience gained so far is restricted to temperatures between 20 and 200°C. In this range the apparatus operates quite satisfactory. Since the block is contained in a Dewar flask and may be easily cooled we see no objections to determinations at temperatures far below zero. (The measuring vessel shown is only a simple model. It may be easily changed in such a way that contact between the substance and surrounding air (moist) is prevented.) As a matter of fact, the apparatus is intended to be used both at high as well as at low temperatures.

ACKNOWLEDGEMENTS

We are much indebted to Mr. W. SCHOON and Mr. C. LANNING, glass-blower and instrument-maker at the Analytical Laboratory of the State University, Utrecht, for their skilful work in making resistance thermometers. Further thanks are due to Mr. C. Z. VAN DOORN, Mr. E. G. BERNS and Mr. C. C. V. D. SPOEL for their assistance during the development of this apparatus.

SUMMARY

A description is given of an apparatus for the determination of heating curves by means of the "thin film" method. The amount of substance used is about 500 mg. The apparatus permits the

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* It is assumed that R_1 and R_2 are approximately equal to R_3.

automatic recording of heating curves with an accuracy of 0.001°C within a range of 0.2°C. By simply resetting a resistance the next following range of 0.2°C may be recorded. Larger ranges may be investigated completely automatically, with a temperature sensitivity inversely proportional to the range, however.

The dimensions of the calorimetric part of the apparatus are discussed. The thermometers used are platinum resistance thermometers having a resistance of about 600 ohms at room temperature. The diameter of the thermometers is about 6.5 mm and their length amounts to 25 mm.

A scheme of the amplification system for recording the temperature and controlling the heating current is presented.

The apparatus may be used from temperatures of from 200°C to far below zero.

RÉSUMÉ

Un appareil pour la détermination des courbes de chauffage par la ,,méthode du film mince" est décrit. La quantité de substance employée est de 500 mg. L'appareil permet l'enregistrement automatique des courbes de chauffage avec une précision de 0.001°C dans un intervalle de 0.2°C. En faisant changer simplement une résistance, on peut enregistrer l'intervalle de 0.2°C suivant. Des intervalles plus grands peuvent être étudiés automatiquement mais, la sensibilité à la température étant cependant inversement proportionelle, à l'intervalle étudié.

Les dimensions de la partie calorimétrique de l'appareil sont discutées. Les thermomètres employés sont des thermomètres à résistance de platine avec une résistance de 600 ohms à température ordinaire. Le diamètre des thermomètres est de 6.5 mm environ, leur longueur de 25 mm.

Un schéma du système amplificateur pour l'enregistrement de la température et le réglage du courant de chauffage est présenté.

L'appareil peut être employé à des températures allant jusqu'à 200°C et jusqu'à bien en dessous de zéro.

ZUSAMMENFASSUNG

Ein Apparat zur Bestimmung von Erhitzungskurven mit Hilfe der ,,Dünnfilmmethode" wird beschrieben. Die benützte Substanzmenge betrug 500 mg. Der Apparat erlaubt die automatische Aufzeichnung von Erhitzungskurven mit einer Genauigkeit von 0.001°C in einem Bereiche von 0.2°C. Durch einfaches Verstellen eines Widerstandes kann der nächste Bereich von 0.2°C registriert werden. Grössere Bereiche können vollautomatisch untersucht werden, wobei aber die Temperaturempfindlichkeit umgekehrt proportional dem Bereiche ist.

Die Dimensionen des kalorimetrischen Teiles des Apparates werden erörtert. Die benützten Thermometer sind Platinwiderstand-Thermometer mit einem Widerstand von ungefähr 600 Ohm bei Zimmertemperatur. Der Durchmesser der Thermometer beträgt ungefähr 6.5 mm, die Länge 25 mm.

Ein Schema des Verstärkungssystems zur Temperaturregistrierung und Regelung des Heizstromes wird vorgelegt.

Der Apparat kann für Temperaturen bis zu 200°C und auch bis weit unter Null angewendet werden.

REFERENCES

[1] W. M. Smit, *Rec. trav. chim.*, 75 (1956) 1309.
[2] S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, 35 (1931) 2091.
[3] W. M. Smit, *Anal. Chim. Acta*, 17 (1957) 23.
[4] M. D. Liston, C. E. Quinn, W. E. Sargeant and G. G. Scott, *Rev. Sci. Instr.*, 17 (1946) 194.

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Motion submitted by Prof. J. G. Aston and carried at the I.U.P.A.C. Symposium on Purity Control by Thermal Analysis, held in Amsterdam, 24th-26th April, 1957.

It is evident that the melting curve (freezing curve) is not always a reliable criterion of purity. Therefore the Symposium on Purity Control by Thermal Analysis recommends, as a result of the meeting, that this fact be recognized. Further, that standard samples known and unknown be submitted to interested laboratories for measurement. Such measurements will serve to test the reliability of the melting (freezing) curve method of purity determination in certain representative cases.

END OF
PAPERS PRESENTED AT THE SYMPOSIUM
ON PURITY CONTROL BY THERMAL ANALYSIS

WET OXIDATION OF ORGANIC MATTER EMPLOYING PERCHLORIC ACID AT GRADED OXIDATION POTENTIALS AND CONTROLLED TEMPERATURES

by

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INTRODUCTION

The destructive oxidation of macro-gram samples of organic compositions is a much used preliminary routine analytical practice[1-2]. Trace element determinations are then applied. The wet oxidation ash concentrate is then the sample for analysis.

The most efficient and routinely employed wet oxidation methods in the destruction of an organic matter[2] as a sample concentration procedure, involve the use of perchloric acid as oxidant. Perchloric acid mixtures with nitric acid, perchloric-nitric-sulfuric acid mixtures, or in some cases perchloric-sulfuric acid mixtures are employed. The proper perchloric acid concentration (60-72%) as the sole oxidant may be used. In these cases a small amount of vanadium or chromium is effective in shortening reaction times. For compositions containing the more readily oxidized ingredients the use of nitric-perchloric acid is most effective. The nitric acid serves to oxidize the easily destroyed organic matter. Subsequent to this oxidation at gradually increasing reaction temperatures, the excess nitric acid is expelled (140-150°C), and perchloric acid completes the removal of remaining organic matter. For samples of organic matter highly resistant to oxidation, mixed perchloric-sulfuric acids may be used to advantage. In such cases molybdenum is effective as catalyst.

The objective in the selection of the proper oxidative composition is governed by the nature of the organic composition serving as sample. By proper selection of the best suited perchloric acid concentration, or the mixed acids selected, and by the use of the proper catalyst, reaction conditions which favor rapid, hazard free, complete destruction of organic matter can be provided. Reaction times in general range from 5 to 30 minutes. The proper reaction apparatus has been standardized[2,3]. Total recovery of the trace element to be determined is assured.

Wet ashing procedures previously described have been widely employed in determination of macro-scale amounts of a given element when present in commercial samples chiefly organic in composition. An example is in the determination of chromium in leather (1 to 10%), or medical catgut (1 to 5%). Further examples are the determination of calcium, magnesium and phosphorus in foods and feeds or the determination of sulfur in rubber, coal or coke.

NEW OBJECTIVES IN THE WET OXIDATION OF ORGANIC MATTER EMPLOYING BOILING CONTROLLED CONCENTRATIONS OF PERCHLORIC ACID

Popular use of perchloric acid in the wet oxidation of organic matter has been somewhat retarded in routine applications by apprehension that such procedures involve violent reaction hazards. The vast number of routine control laboratory analyses of this type now performed daily in a number of chemical industries, in reality discount this viewpoint of accompanying hazards. The present work is designed to demonstrate that the redox potential of perchloric acid can be effectively controlled. This completely eliminates the possibility of hazard in the rapid destruction of organic matter of selected type samples. The recovery of the elements to be determined in the wet ash residue is quantitative. The process is not complicated by the presence of excess perchloric acid in the carbon free completed digestion. Controlled oxidation potentials are maintained and their magnitude adapted to the requirements in each particular case. All possible reaction hazard is thus eliminated. These oxidative reaction intensities of perchloric acid are maintained through digestion under refluxing conditions. Reaction types experimentally explored include cellulose, proteins and carbohydrates or products predominantly of this composition.

THE VARIATION IN BOILING POINT OF 50 TO 70 PER CENT PERCHLORIC ACID

The perchloric acid-water azeotrope (72.5 per cent $HClO_4$), has an oxygen content of 46.4 per cent. Most of this oxygen content is made available at its boiling point. With perchloric acid composed of lower hydrate forms ($2HClO_4 \cdot 5H_2O$, $HClO_4 \cdot 3H_2O$, and $2HClO_4 \cdot 7H_2O$), the available oxygen decreases and the boiling point lowers. At concentrations below 50 per cent, aqueous perchloric acid at its boiling point is practically zero in oxygen availability.

By control of acid concentration at selected levels, the redox potentials may be simultaneously graded and controlled. The negligible oxidation potential of boiling perchloric acid at 50 per cent concentration may be slowly and steadily increased as the acid concentration is augmented. At 70 to 72.5 per cent boiling solutions of perchloric acid make oxygen readily available. In the presence of readily oxidizable materials such solutions may promote uncontrolled reaction intensities. Employing controlled perchloric acid concentrations, reactions of oxidation may be regulated to give a wide variety of oxidation potentials. Reaction intensities from 0.8 to 0.85 volts for boiling 50 per cent perchloric acid, with all gradations in ascending values to 2.0 volts or higher for 73.6 per cent acid strength (the exact $HClO_4 \cdot 2H_2O$ hydrate), may be precisely established.

Apparatus design to maintain selected concentrations of perchloric acid throughout a given oxidation process has been previously described. Controlled acid concentration results from the use of the reflux condenser principle. Acid concentration is thus unaltered throughout a given period of reaction. Means are also provided for increasing the active acid concentration at any time interval. Such conditions are provided through apparatus design permitting withdrawal of accumulated reflux during a given time interval. By such operation the perchloric acid concentration in any reaction may be progressively increased over the range 50 to 72.5 per cent.

Practical oxidation reaction intensities illustrative of graded potential control may be informative.

1. Hypophosphorous acid is not oxidized by boiling 30 per cent perchloric acid. Its oxidation is instantaneous and intensely violent in contact with hot 72.5 per cent perchloric acid.

2. Boiling 50 per cent perchloric acid converts Fe^{+2} to Fe^{+3} at very slow rate (90 per cent oxidation, approximately, in a ten-minute interval). Under these conditions the redox potential is estimated to be 0.8 to 0.85 volts.

3. Boiling 50 per cent perchloric acid does not oxidize VO^{+2} to VO_3^-. Thus the redox potential is indicated to be less than 1.0 to 1.1 volts.

4. Boiling 57.5 per cent perchloric acid slowly oxidized the vanadyl ion to vanadate. The redox potential is thus approximately 1.3 to 1.4 volts.

5. Boiling 60 per cent perchloric acid readily oxidizes the vanadyl ion to vanadate. The oxidation potential required is approximately 1.45 to 1.5 volts.

A convenient, and sufficiently accurate method, for the approximate determination of the concentration of perchloric acid in aqueous solutions is by the determination of the boiling point. The increase in boiling point as a function of acid concentration is given in the plot of data shown in Fig. 1, of the data given in Table I.

The acid concentrations given in Table I and the graph of Fig. 1 were determined by titration with standard sodium hydroxide (averaged duplicate determinations). The standard alkali was evaluated by the use of the exact dihydrate of perchloric acid

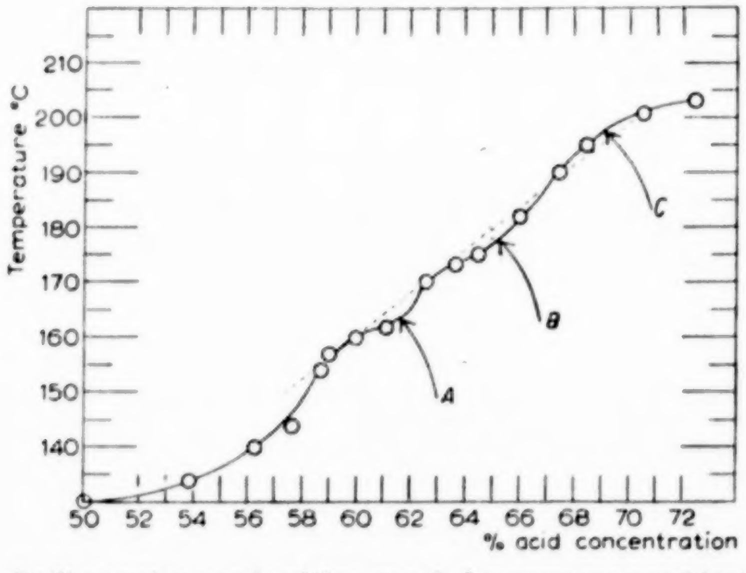

Fig. 1. Boiling point-composition graph for aqueous perchloric acid.

($HClO_4 \cdot 2H_2O$) as primary standard. Accurately weighed samples of this standard in small glass stoppered vials were placed in beakers, 150-200 ml of water added, and titrated by the alkali employing bromthymol blue as indicator. By like procedure, stock solutions of varying concentrations of perchloric acid were then established in acid content.

The boiling point of the stock solutions was then determined. The apparatus consisted of a 125 ml Erlenmeyer flask surmounted by a 20 cm reflux condenser, the union of flask and condenser consisting of a 24/40 standard taper flask to condenser ground joint. A 20 ml sample of acid was employed with addition of carborundum boiling chips to prevent super-heating. The thermometer was suspended within the condenser and the mercury well completely immersed in the boiling acid.

Results are tabulated in Table I.

TABLE I

THE BOILING POINT OF VARIOUS CONCENTRATIONS OF AQUEOUS PERCHLORIC ACID

Acid Concn %	*B.p.* °*C*	*Acid Concn.* %	*B.p.* °*C*	*Acid Concn.* %	*B.p.* °*C*
50.0	130	59.2	157	66.0	182
53.9	135	60.1	160	67.5	190
56.3	140	62.6	170	68.4	195
57.7	154	63.8	173	70.6	201
58.8	157	64.5	175	72.5[a]	203

[a] The $HClO_4$-H_2O azeotropic concentration.

It will be observed from Fig. 1 that the increase in boiling point with increase in acid concentration is not a straight line function. This results from the presence of a number of fixed hydrates of perchloric acid. The relationship is practically a straight line function from 60 to 70% perchloric acid concentration. The use of the data of Fig. 1 is sufficiently accurate to establish acid concentrations of required control limitations to be applied in the procedures being described.

APPARATUS DESIGN

A slightly modified BETHGE apparatus[3] is employed. A line drawing is shown in Fig. 2.

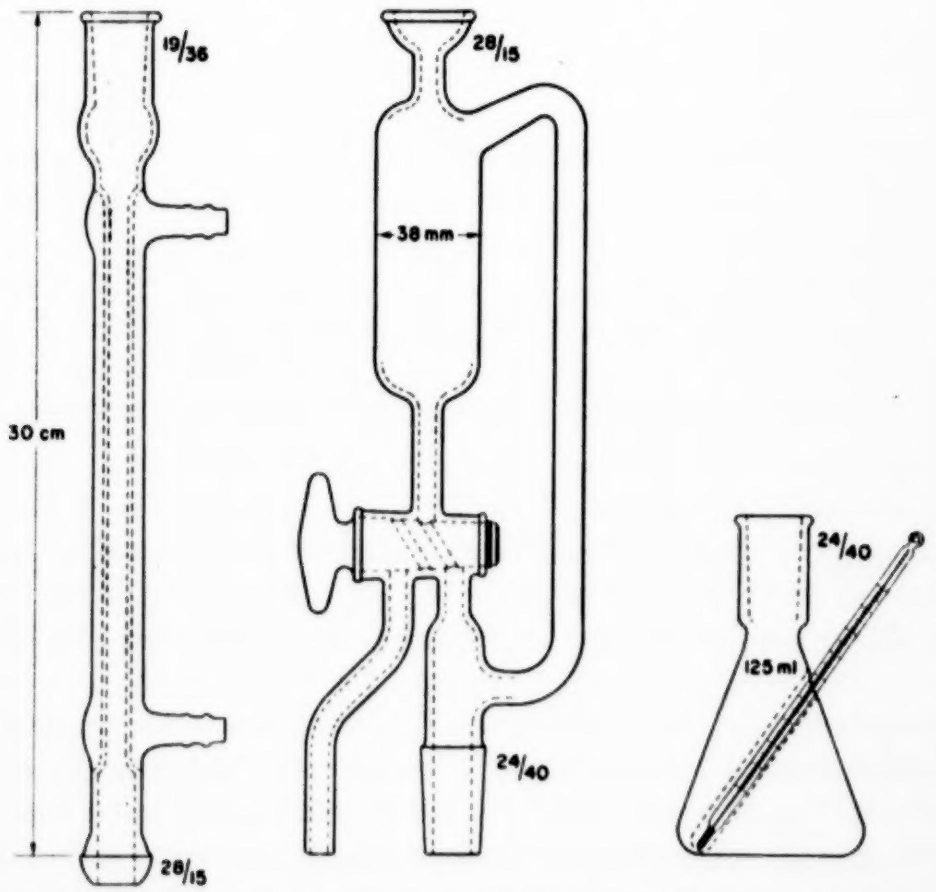

Fig. 2. Reaction assembly for wet oxidation employing graded potential control (no stopcock lubricants required).

The reaction flask is a 24/40 standard taper top, 125 ml Erlenmeyer flask (with or without thermometer well), as shown with thermometer in place. The refluxing action is provided using two parts. The air cooled condenser and retaining reflux reservoir and three-way, 4 mm stopcock at the lower extremity provides a double entry of vapor from ebullition. Either vapors pass through the stopcock properly set, or they bypass the stopcock up through the side tube vent. With the air condenser stopcock closed, the condensate passes through the side tube into the refluxing reservoir to be collected or withdrawn (through proper adjustment of the stopcock), for delivery to a suitable receiving vessel.

Any reflux not condensed, air cooled, is collected in the 20 mm water cooled condenser and collected in the stopcock subtended air cooler condenser. The ball and socket standard ground joint between the water cooled and air cooled condensers provides for its ready removal in disassembling and is firmly held in place without clamp support employing a customary double U spring clamp support holding the ground joint firmly in place.

A single ring stand clamp firmly attached to the neck of the reaction flask, together with the support provided by the 24/40 ground joint between the reaction flask and air condenser, obviates further clamp supports to hold the three piece assembly firmly in place.

The reaction flask may be heated over a wire gauze with a gas burner. The use of an adjustable heat electric hot plate may be preferred.

With the stopcock adjusted to return the reflux condensate to the reaction flask, the starting concentration of boiling perchloric acid may be maintained constant throughout any given reaction period.

Closing the stopcock permits collection of any desired measure of condensate with accompanying increase in reactant acid concentration. The extent of this adjustment can be followed by observation of the thermometer, if provided. In its absence, the volume of condensate can be measured and withdrawn after which the air condenser stopcock can be readjusted to again return condensate from the boiling reaction flask.

By such manipulation the perchloric acid concentration may be augmented stepwise over the effective oxidation range 50-72.5 per cent. If desired, the withdrawn condensate may be returned to the reaction flask through the opened stopcock of the water cooled condenser and the original reaction conditions restored.

REACTION CHARACTERISTICS

The oxidation of cellulose serves admirably as a characteristic reaction illustration. Reaction data are given in Table II.

TABLE II

GRADED POTENTIAL OXIDATION OF CELLULOSE (S. AND S. ASHLESS PAPER) OR RAFFIA

[20.0 ml of $HClO_4$-0.01 g $(NH_4)_3VO_4$ catalyst-Boiling temperature]

Sample 0.8 g	*$HClO_4$ concn. %*	*Time for complete oxidation minutes*	*Remarks*
Cellulose	50.0	375	Reaction still incomplete
,,	57.7	60	Excessive foaming
,,	60.1	52	No excessive foaming
,,	62.6	45	—
,,	64.0	17	—
,,	66.0	9	—
Raffia	64.5	18	Same type oxidation as pure cellulose
,,	66.0	7	—

From the examination of the data of Table II, it will be observed that the oxidation potential of 50 to 60 per cent perchloric acid at boiling point 132 to 160 degrees C is not sufficient to rapidly oxidize the chocolate brown degradation products formed initially as the reacting acid attains the boiling temperature. Without the use of vanadium as catalyst, even at 60 per cent acid concentrations, the oxidation rate is prohibitively slow. At concentrations of acid between 62.5 and 65.0 per cent the potential has sufficiently augmented to bring about rapid oxidation ($2HClO_4 \cdot 7H_2O$ to $HClO_4 \cdot 3H_2O$ hydrate range). At 66.0 per cent acid strength the reaction time is so limited that to exceed this acid concentration would permit the rate to get out of hand. At 72.5 per cent acid concentration the oxidation would occur with violence.

The destruction of samples such as raffia, dried hay or straw or other types predominantly consisting of cellulose would be predicted to follow the same trends as those indicated in Table II.

DIFFERENTIAL OXIDATIONS EMPLOYING PERCHLORIC ACID

A favorable property of perchloric acid as a graded potential oxidant, previously demonstrated, consists in the fact that it is a good solvent for cellulose, sugars of all types, as well as protein predominating compositions such as leather, collagen, wool, and many other chemical compositions. This has the advantage that the organic matter to be oxidized is instantly thoroughly dispersed in the oxidation medium even before a temperature is attained which produces fragmentation of the sample. This at the boiling temperature produces a semi-charred carbonaceous accumulation during oxidative elimination. Flocks of carbonaceous degradation matter result, which are dark in color but are far removed from the character of reaction products which result from the substitution of sulfuric acid for perchloric acid as oxidant. These flocks of carbonaceous compositions are much more extended in active surface for reaction and are of such density that they easily float suspended in the reaction medium which has a density of less than 1.6.

A very great advantage provided by perchloric acid as oxidant also consists in the ready solubility of such elements, if present, as calcium and others which, following $HClO_4$ oxidation, remain in solution throughout the digestion. Phosphorus, if present, is quantitatively retained together with all elements, which, even if volatile, under ordinary conditions are retained through the influence of reflux return to the reaction medium.

Complex organic compositions may be fractionally destroyed. An example is that of the destructive decomposition of wool. By control of the perchloric acid concentration the destruction of organic matter can be regulated in such manner as to leave unoxidized, an oily or fat-like oxidation resistant material which continues to be collected in the condensate. This product cannot be oxidized until in contact with boiling perchloric acid of increased concentration. Its isolation in the digestion as described can be provided by withdrawing condensate and replacing it by an equal amount of water to maintain an unincreased oxidation potential throughout the digestion.

The digestions as described, besides requiring no fume hood for work in the open laboratory, also provide for the removal of most of the excess perchloric acid preliminary to the determination of sought ingredients in the wet ash residue. Although such digestions involve considerable (1/2 to 1 inch) foam formation during the early stages of the reactions, which causes carbon flocks to attach themselves to the inner walls of the reaction flask, their removal is not troublesome. When the principal reaction of oxidation is complete at a fixed perchloric acid concentration, the reflux return to the reaction flask is cut off and the reaction acid rapidly concentrates (2 to 4 minutes), to the composition of 72.5 per cent at which concentration the vapor phase is rapidly reactive in the destruction of foam deposited carbon flocks.

GRADED POTENTIAL OXIDATION OF WOOL

A gram sample of wool yarn was digested in 20 ml of 64.5 per cent perchloric acid using 0.01 g of $(NH_4)_3VO_4$ as catalyst. Reaction temperature control was applied by withdrawal of collected samples of distillate. The results are given in the data of Table III.

TABLE III

GRADED POTENTIAL OXIDATION OF WOOL

Reaction time[a] minutes	*$HClO_4$ concn. %*	*Temp. °C*	*Reaction color*	*Remarks*
3	64.5	175	Dark red brown	No foaming
5	64.5	175	,, ,, ,,	—
10	64.5	175	Light red brown	—
20	64.5	175	Orange	Oily condensate
24	66.0	185	Light yellow	—
26	66.0	185	,, ,,	No more oily condensate
28	66.0	185	Light green	Return collected condensate
30	68.0	193	Light yellow	Reaction complete

[a] Refluxed condensate collected at 22 and 28 minutes reaction time.

From an examination of the data of Table III attention is called to the fact that at no stage of the digestion is there any char formation, foaming or formation of insoluble products. The destruction of organic matter is not complete at acid concentrations of 64.5 per cent. An oily fraction continues to pass into the condenser mechanism and return to the reaction flask. As indicated 66 per cent acid at boiling point 185°C is effective in the oxidation of this oily decomposition product. This oxidation is noticeably exothermic and rapid. The isolated reflux condensate is shown to have a small amount of organic matter contamination and upon return to the reaction flask this is indicated by color change from light yellow (due to the oxidized vanadium catalyst), to light green. Final complete oxidation is accompanied by the return of the vanadate yellow color.

This reaction was duplicated starting with 61.0 per cent perchloric acid and at 165°C was allowed to proceed for 8 minutes. Reflux reaction was cut off in one minute intervals, for periods of 1 minute duration, followed by 1 minute boiling. By this operation the oxidation was complete in 15 minutes. By this same procedure, and allowing the reaction to progress until the color is reddish orange, then increasing the acid concentration from 65 per cent to 66-68 per cent through the retention of refluxing condensate, the following types of sample (gram samples), dried beef, longhorn cheese, dried apricot and vegetable tanned leather, were wet ashed. The times for complete reaction were respectively 17, 20, 26, and 26 minutes.

GRADED POTENTIAL PERCHLORIC ACID-SULFURIC ACID OXIDATIONS

For use in the destructive oxidation of organic compositions which require potentials greater than that provided by 72.5 per cent perchloric acid, mixtures of sulfuric and perchloric acid may be employed. The use of the apparatus described provides for the use of H_2O-$HClO_4$-H_2SO_4 mixtures of their lower oxidation potential followed by the stepwise withdrawal of distillate. At each withdrawal the oxidation potential is augmented and finally can result in perchloric acid potentials due to an effective perchloric acid concentration from 72.5 per cent to, and above 85 per cent. The advantage consists in the adjustment of the oxidation potential to the desired magnitude stepwise.

GENERAL DESCRIPTIVE PRACTICAL APPLICATIONS

It would be out of place to carry out any considerable number of graded potential wet oxidation reactions to be described in connection with this project, in the interests of brevity. For any practical application a prospective user will be able to explore the reaction characteristics of a given sample following the directions as given. Larger samples than one gram are not generally required since the determination of such trace elements as Fe, Cu, P and other elements can be carried out using spectrophotometric procedures of a very high order of sensitivity. By proper adjustment of reaction conditions the procedures are without hazard, may be applied without the use of a fume hood and are not much more time consuming than previously found in wet oxidations performed without close control of the oxidation potential of the mixed $HNO_3 + HClO_4$ commonly employed. The process as outlined enables one to unequivocally prove the presence or absence of any possible loss of the element for determination by volatilization by withdrawing refluxed distillate followed by its appropriate examination. Provided the element sulfur is to be determined following wet oxidation by the method as described, the addition of nitric acid is required. If used, means are at the same time at hand for its subsequent removal by withdrawing condensed distillate. The sulfuric acid content of the residual wet ashing flask contents can be readily determined without interference from the perchloric acid content. Such determination as in the case of rubber would appear to be attractive.

CATALYTIC REACTION CHARACTERISTICS

The three most effective catalysts which may be employed in wet oxidations are vanadium, chromium, and molybdenum. Additions of the catalysts in amounts of 5 to 6 mg per wet ashing operation reduces reaction time to one-half to one-third or less that required under digestions in the absence of catalysts.

For oxidations at 60.0 to 68.0 per cent perchloric acid vanadium as catalyst serves most effectively. For reactions at 68.0 to 72.5 per cent perchloric acid concentration either vanadium or chromium are effective. For mixed perchloric acid-sulfuric acid digestions, molybdenum is very effective. The oxidized catalyst owes its effect to its continuous reduction by organic matter and re-oxidation by the acid of the particular process involved. If desired, Cr as catalyst can easily be removed from ash residue as volatile CrO_2Cl_2 through the use of added hydrochloric acid to the boiling ash residue.

THRESHOLD PERCHLORIC ACID OXIDATION POTENTIAL

The oxidation of a number of types of organic compositions and natural products is not practical employing perchloric acid alone as oxygen donor. The range of acid concentration and temperature within which a rapid, smooth, and controlled rate of oxidation is provided, is too narrow to be trustworthy. Over and above such a threshold acid concentration, by a narrow margin of perchloric acid concentration, the rate of oxidation becomes, if not actually violent, none the less uncontrolled.

An example of this type reaction is the destructive wet oxidation of rubber.

A one gram sample of pure gum rubber when digested at the boiling point of 62.5 per cent perchloric acid (170°C), was virtually unattacked. The effect was only that of blackening the rubber granules of the sample. The use of a small addition of vanadium as catalyst was ineffective.

By duplicate attempt employing 64.5 per cent perchloric acid with vanadium, the reaction time for complete oxidation was 24 hours boiling at 175°C.

Under the same conditions employing 66 per cent perchloric acid (20 ml), 10 mg of ammonium vanadate, and at a reaction temperature of 184°C, oxidation, while progressing materially, was not sufficient to predict completion in a satisfactory time limit. After 60 minutes refluxing in an attempt to bring the reaction to completion, a 0.5 ml of distillation reflux was collected. At this point the unoxidized rubber caught fire within the reaction flask and the organic matter was completely carbonized in a time interval of approximately 10 seconds. Narrow threshold oxidation potentials in the process as described call for modification in procedure.

OXIDATION OF PURE GUM RUBBER BY MIXED NITRIC-PERCHLORIC ACID

The problem of the practical oxidation of the type material having a narrow range threshold perchloric acid oxidation potential, may be admirably solved through the addition of nitric acid.

A one gram sample of pure gum rubber was added to a mixture of 20 ml of 63.75 per cent perchloric acid, 5 ml of 67 per cent nitric acid and 10 mg of ammonium vanadate in the same apparatus previously employed.

At 50 seconds heating the reaction flask was full of brown fumes due to the oxidation of rubber by the nitric acid of the digestion mixture. At 2.5 minutes all rubber granules underwent dissolution, the reaction mixture was orange in color, and gas evolution products produced 25 mm of foam. In 4 minutes all the nitric acid reaction was complete as indicated by the absence of brown fumes. The reaction mixture had a yellow color. At the 5 min interval the refluxing distillate being returned to the reaction flask was cut off. At 6 minutes, the reaction mixture was turbid and green in color. The reflux condensate returned to the reaction flask was again collected for 1 minute and then returned to the reaction flask at the seven minute interval. The collection of reflux was again resumed and at 10 minute reaction time the oxidation of the rubber was complete.

Any possibility that the collected reflux of mixed nitric and perchloric acids contained evolved reaction products which should be retained in the wet ash residue in the digestion flask, can be separately determined by special withdrawal and examination. The collected reflux may again be returned to the reaction flask and the second distillation of the more volatile components of the reaction again distilled out.

By the use of mixed nitric-perchloric acid wet ashing procedures, the number of types of organic matter that can be digested is extended at the expense of more elaborate demand for attention to the process. The number of digestions which can be provided without the use of added nitric acid and which require no individual attention make their use more attractive.

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NOTEWORTHY ASPECTS OF PERCHLORIC ACID IN ITS USE AS OXIDANT IN WET ASHING PROCEDURES

A number of organic reducing agents may be rapidly and completely oxidized without uncontrolled reaction or violent aspects. Examples are oxalic and formic acids. In contact with 72.5% perchloric acid either hot or cold the reaction is that of liberation of CO_2 as decomposition product. If 5 g of oxalic acid dihydrate are added to boiling 72.5% perchloric acid approximately 9-10 min are required to complete the oxidation in the presence of 15-20 ml of the boiling acid oxidant. The addition of 0.1 mg of vanadium as catalyst to the digesting mixture doubles the rate and by addition of approximately 0.5 mg of vanadium the reaction is complete in 1-2 minutes. Formic acid in the form of added sodium formate is correspondingly more actively destroyed.

The wet ashing oxidation of samples predominating in protein such as dried beef, medical catgut, or vegetable tanned leather is accomplished with the absence of any deposition of carbonaceous products although the reaction mixture in some cases darkens the sample at no time fails to remain completely dissolved in the hot perchloric acid. Flocks or fluffy granules of carbonaceous degradation products are formed in the oxidation of cellulose or sugar by the process previously described but are rapidly removed as the controlled concentration of perchloric acid completes their oxidation. With leather and meat protein oxidations vanadium and chromium are found to be efficient catalysts, particularly vanadium. For these digestions 66-68% perchloric acid is adequate. For cellulose or sugars 66%, preferably 65%, or somewhat less, is practicable. Aromatic ring nitrogen compositions such as quinoline or the phenanthrolines require perchloric-sulfuric acid combinations for destructive oxidation. Such acid mixtures can be employed under reflux at controlled oxidation potential following the previously outlined use of the apparatus of Fig. 2. Samples such as coal and coke or adsorbant charcoal require chromium or vanadium catalysts for oxidation with use of 72.5% boiling perchloric acid. Materials such as Teflon are completely without degradation in boiling 72.5% perchloric acid. Means have thus been provided for many types of wet ashing procedures for which a little careful experimentation will lead to control of reaction procedures which are rapid, efficient and precise, accompanied by freedom from apprehension that uncontrolled reactions ensue.

SUMMARY

A new modified apparatus has been described for use in the wet ashing of organic matter using boiling, controlled concentrations of perchloric acid as oxidant. Typical operative procedures and manipulations are discussed and a number of direct applications to various types of materials has been demonstrated. Cellulose, proteins, and sugars and materials predominating in these types, have been selected as best applicable examples. Perchloric acid concentrations tested were from 55-68 per cent and intermediate concentrations. The procedures described provide conditions which though effective are less encumbered by the implication of hazard often charged against 70-72.5 per cent perchloric acid in similar previously published and widely applied procedures.

RÉSUMÉ

Un nouvel appareil est décrit pour la minéralisation de matières organiques, en utilisant comme oxydant l'acide perchlorique à ébullition et à concentrations contrôlées. Le mode opératoire et les manipulations sont discutés, et un certain nombre d'applications sont faites avec des substances variées. La cellulose, les protéines et les sucres et d'autres substances qui se composent principalement de ces matières ont été choisis comme exemples. Les concentrations d'acide perchlorique utilisées ont varié de 55 à 68%. Les méthodes décrites offrent des conditions qui bien qu'efficaces ne sont pas considérées comme dangereuses contrairement aux procédés utilisant l'acide perchlorique à 70-72.5%, procédés déjà publiés et souvent utilisés.

ZUSAMMENFASSUNG

Ein neuer modifizierter Apparat zur nassen Veraschung von organischem Material mit kochender Perchlorsäure von bestimmter Konzentration als Oxydationsmittel, wurde beschrieben. Arbeitsgang und Handlungen werden erörtert und eine Anzahl direkter Anwendungen auf verschiedene Arten von Materialien werden beschrieben. Zellulose, Proteine und Zucker, und Materialien welche hauptsächlich aus diesen Stoffarten bestehen wurden als Musterbeispiele ausgesucht. Perchlorsäure-Konzentrationen von 55 bis 68% wurden angewendet. Die Versuchsbedingungen der beschrieben Verfahren sind zweckmässig und doch weniger gefährlich als diejenigen von früher beschriebenen Verfahren, welche 70-72.5%-ige Perchlorsäure verwenden.

REFERENCES

[1] G. FREDERICK SMITH, *Ind. Eng. Chem., Anal. Ed.*, 18 (1946) 257.
[2] G. FREDERICK SMITH, *Anal. Chim. Acta*, 8 (1953) 397.
[3] P. O. BETHGE, *Anal. Chim. Acta*, 10 (1954) 317.

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METAL-ORGANIC COMPLEXES OF ANALYTICAL SIGNIFICANCE

I. THE STABILITIES OF COMPLEXES OF BIVALENT METALLIC IONS WITH ANTHRANILIC ACID AND ITS DERIVATIVES

by

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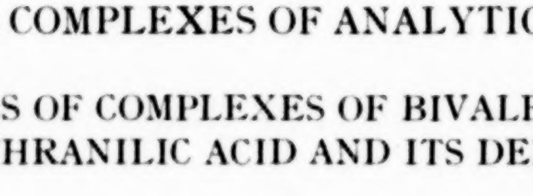
Anthranilic acid and several of its derivatives react with an extensive range of bivalent metallic ions. In particular, the bivalent ions of cadmium, cobalt, copper, iron, lead, manganese, nickel and zinc form insoluble chelate compounds represented by the formula



where M is the metallic ion. In Table I the reactions of the acid and some of its derivatives with the cations, in neutral solution, are summarised.

TABLE I

Reagent	*Ion*							
	Cd^{+2}	Co^{+2}	Cu^{+2}	Fe^{+2}	Pb^{+2}	Mn^{+2}	Ni^{+2}	Zn^{+2}
Anthranilic acid	P	P	P	P	P	P	P	P
5-Bromoanthranilic acid	P	P	P	P	P	P	P	P
5-Nitroanthranilic acid	X	X	P	X	P	X	X	X
5-Iodoanthranilic acid	P	P	P	P	P	P	P	P
5-Sulphoanthranilic acid	X	X	C	C	P	X	X	X
5-Methylanthranilic acid	P	P	P	C	P	X	X	P
3:5-Dibromoanthranilic acid	P	P	P	P	P	X	P	P
N-Methylanthranilic acid	P	P	P	P	P	P	P	P
N-Acetylanthranilic acid	X	X	P	X	P	X	X	X

P = precipitate
C = colour change but no precipitate
X = no apparent reaction

Investigation of the stabilities of the complexes formed in these reactions presents some difficulty. The most frequently used methods for obtaining information on stability rely on pH measurements[1], polarographic measurements[2], or absorption spectra determinations[3]. However, none of the chelates produced in these reactions is sufficiently soluble in any simple solvent to allow any of the more conventional methods to be used.

Information regarding stability could be derived from electrolytic data. An electrolytic cell was therefore devised which operated under the desired conditions, and stability constants were calculated from the E.M.F. values obtained.

The following reasoning is utilised for this purpose. If the reaction

$$A + B \rightleftharpoons C + D \quad \ldots \ldots \quad (1)$$

takes place in an electrolytic cell, then

$$E = E_0 - \frac{RT}{NF} \cdot \ln \frac{a_C \times a_D}{a_A \times a_B} \quad \ldots \ldots \quad (2)$$

where E is the measured E.M.F. of the cell, E_0 is the standard E.M.F., and a is the relevant activity.

If the activities of all the reacting substances are unity, then

$$E = E_0 \quad \ldots \ldots \quad (3)$$

In the reaction

$$M + 2\,HR \rightleftharpoons MR_2 + H_2 \quad \ldots \ldots \quad (4)$$

where M represents a bivalent metal, and HR represents anthranilic acid or a related compound, conditions may be arranged to conform to the equation

$$M_{(solid)} + 2\,HR_{(solid)} \rightleftharpoons MR_{2(solid)} + H_{2(gas)} \quad \ldots \ldots \quad (5)$$

For such a reaction the three solid components are assumed to be in their standard states, and so their activities are unity. Hydrogen may be assumed to behave as a perfect gas over small pressure changes in the neighbourhood of one atmosphere, so that its activity will be unity when its partial pressure is one atmosphere. Therefore if a correction is made for variation in pressure, all the components will be in their standard states, and equation (2) becomes

$$E_0 = E + \frac{RT}{NF} \cdot \ln \frac{P - P'}{760} \quad \ldots\ldots (6)$$

where P is the atmospheric pressure, and P' is the vapour pressure of the solution, so that P—P' represents the partial presssure of hydrogen.

If the solutions are very dilute, the vapour pressure of the solvent (water) may be used as an approximation to P'.

If E can be measured then E_0 may be determined. From this it is then possible to calculate

ΔF_0, the standard free energy change;
log K, where K is the equilibrium or stability constant;
ΔH_0, the standard heat content change; and
ΔS_0, the standard entropy change.

The relations used for these calculations are

$$NFE_0 = -\Delta F_0 \quad \ldots\ldots (7)$$

$$-\Delta F_0 = RT \ln K \quad \ldots\ldots (8)$$

$$\frac{\mathrm{d} \ln K}{\mathrm{d}T} = \frac{\Delta H_0}{RT^2} \quad \ldots\ldots (9)$$

$$\Delta F_0 = \Delta H_0 - T\Delta S_0 \quad \ldots\ldots (10)$$

In practice the values of ΔF_0 are calculated from E_0 by (7), ΔH_0 is determined from a graph of $\Delta F_0/T$ against $1/T$, and ΔS_0 is determined from a graph of ΔF_0 against T.

When investigating chelation in relation to analytical chemistry, the reaction occurring in solution when a bivalent metal is involved, which is

$$\mathrm{M^{+2} + 2\,HR + 2e \rightarrow MR_2 + H_2} \quad \ldots\ldots (11)$$

is more significant than that represented by equation (4), and it is reaction (11) which is normally studied in other investigations of stability.

Now if ΔF_0 for the reaction

$$\mathrm{M \rightarrow M^{+2}} \quad \ldots\ldots (12)$$

is X, and the measured ΔF_0 for reaction (4) is Y, these may be combined to give, for equation (11)

$$\Delta F_0 = Y - X \quad \ldots\ldots (13)$$

Similar relationships exist for the ΔH_0 and ΔS_0 values for the two reactions.

Values of ΔF_0, ΔH_0 and ΔS_0 for the ionisation of the bivalent metals represented by equation (12) are available in the literature[4]. Consequently ΔF_0 (or log K), ΔH_0

and ΔS_0 values can be derived for reaction (11), the reaction between the metallic ion and the chelating agent in solution.

ΔF_0 (or log K) is a measure of the overall stability of the chelate.

ΔH_0 is a measure of the bonding energy.

ΔS_0 is a measure of the entropy effects contributing to the stability of the chelate.

APPARATUS

The cell (Fig. 1) consists of a glass container with a close-fitting rubber bung which carries a hydrogen inlet and outlet and the electrodes. Each electrode (Fig. 2) consists of a narrow glass tube into which is sealed about 2-3 cm of platinum wire to which is welded a piece of platinum foil 10 mm^2. The electrode is held in a small rubber bung which fits tightly into a glass tube. This, in turn, passes through the bung of the cell. The anode is plated with the metal under investigation. The (hydrogen) cathode is platinised. The electrolyte is a saturated aqueous solution of the chelating reagent, say, anthranilic acid.

In this cell there is no boundary between two electrolytes, and since the solution is saturated there is no concentration gradient. When an E.M.F. is applied across the two electrodes the metal anthranilate, which is almost completely insoluble in water, is deposited on the metal electrode. Therefore there is now present in the cell (i) solid metal, (ii) solid chelating reagent, (iii) solid chelate, and (iv) gaseous hydrogen, and the conditions are those demanded by equation (3).

EXPERIMENTAL

The cell was assembled, and hydrogen was passed through it slowly for three hours. An external E.M.F. was then applied in order to form the chelate, the conditions being those shown in Table II. The hydrogen electrode was replaced by a fresh platinised electrode, and the cell was placed in a thermostat. After at least three hours had passed, readings of the E.M.F. of the cell were taken at intervals until a constant value was obtained. Measurements were made over a range of 40°C, the temperature being controlled to within 0.2°C.

The electrode used for the formation of the chelate was not used for the determination of the E.M.F. of the cell in case any deterioration of the surface had resulted from the application of the external E.M.F.

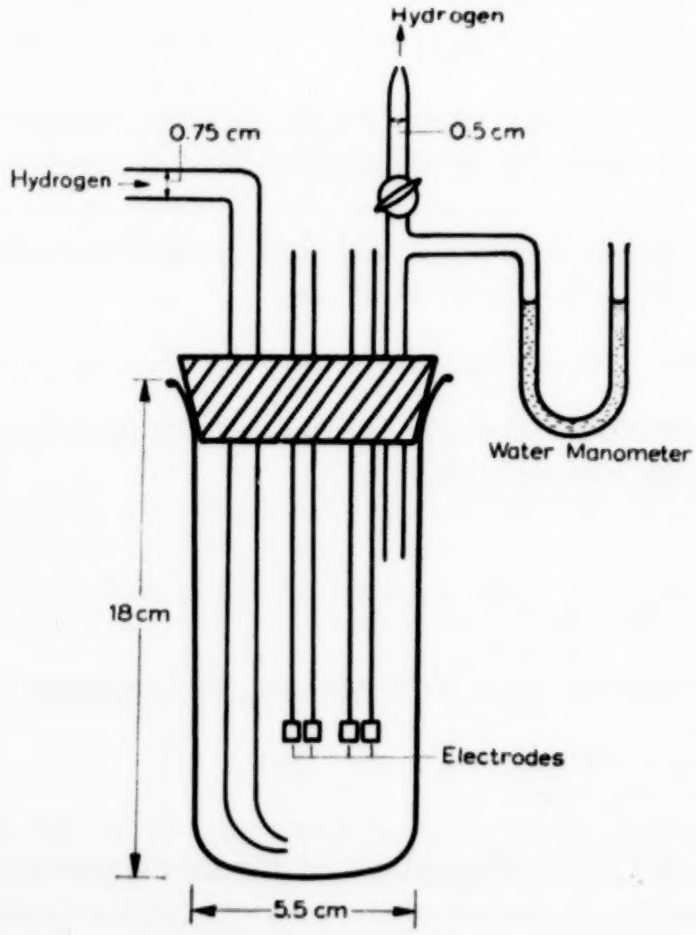


Fig. 1. Electrolytic cell.

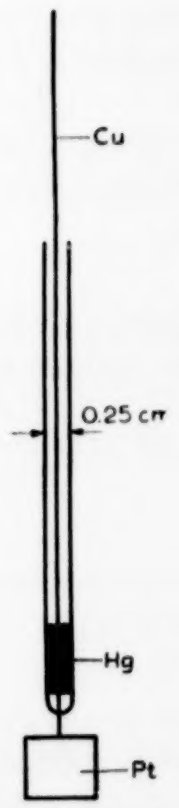


Fig. 2. Electrode.

TABLE II

Chelate	*Conditions*		
	Voltage	*Time, min*	*Current mA*
Cadmium anthranilate	240	25	50
Cobalt anthranilate	120	60	70
Copper anthranilate	120	30	20
Lead anthranilate	240	30	70
Nickel anthranilate	240	120	40
Zinc anthranilate	120	10	30
Copper 5-bromo-anthranilate	120	60	15
Copper 3:5-dibromo- ,,	120	45	25
Copper 5-iodo- ,,	120	15	70
Copper N-methyl- ,,	120	25	40
Zinc 5-bromo- ,,	120	20	20

RESULTS

(a) Variation of the cation: The effect on stability of variation of the cation was studied through measurements on the chelates of a range of cations with anthranilic acid. The experimental results, which are in each case the average of several determinations, and the values calculated from them, are given in section (i) of Table III.

TABLE III

	Chelate	*Reaction (4)*			*Reaction (11)*			
		ΔF_e, 25°C kcals	ΔH_e, kcals	ΔS_e, cals/°	ΔF_e, 25°C, kcals	log K	ΔH_e, kcals	ΔS_e, cals/°
(i)	Cd anthranilate	+12.84	+3.49	−30.93	+31.42	−23.02	+20.79	−35.23
	Co ,,	+1.29	+14.39	+41.47	+13.60	−9.96	+30.49	+64.23
	Cu ,,	+14.14	+23.39	+29.64	−0.39	+0.29	+8.00	+30.11
	Pb ,,	+0.98	+24.52	+82.49	+5.71	−4.18	+24.13	+61.68
	Ni ,,	+0.66	—	—	+11.69	−8.42	—	—
	Zn ,,	−6.60	−24.52	−59.72	+28.58	−20.93	+11.89	−55.54
(ii)	Cu anthranilate	+14.14	+23.39	+29.64	−0.39	+0.29	+8.00	+30.11
	,, 5-bromo-anthranilate	+20.17	+52.52	+108.6	+4.64	−3.40	+37.13	+109.1
	,, 3:5-dibromo- ,,	+20.36	+34.79	+45.84	+4.83	−3.54	+19.40	+46.31
	,, 5-iodo- ,,	+12.86	+29.17	+51.11	−2.92	+2.14	+13.78	+51.58
	,, N-methyl- ,,	+18.88	+46.74	+93.84	+3.35	−2.45	+31.35	+94.31
(iii)	Zn anthranilate	−6.60	−24.52	−59.72	+28.58	−20.93	+11.89	−55.54
	,, 5-bromo-anthranilate	−27.42	−64.24	−122.4	+7.76	−5.68	−27.81	−118.2

(b) Variation of the structure of the reagent: The effect of variation of structure was studied by investigating the stabilities of the chelates formed with copper by a range of derivatives of anthranilic acid. Copper was chosen since the qualitative tests indicated that it was one of the most reactive of the cations studied. The results are given in section (ii) of Table III.

In an extension of this work the effect on zinc chelates of replacement of anthranilic by 5-bromoanthranilic acid was also investigated. The results are given in section (iii) of Table III.

DISCUSSION

(a) Variation of the cation: The stabilities of all the anthranilates are very low, the copper chelate being the only one which shows a positive value for log K. The order of decreasing stability is

$$\mathrm{Cu} > \mathrm{Pb} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn} > \mathrm{Cd}$$

which is similar to the order of stability found for many other chelates[5]. In the transitional elements (that is, omitting lead from the general discussion) the stabilities are apparently related to the second ionisation potentials, a relationship which has been observed for other chelates[6]. It has been suggested that this correlation is due to the fact that the relative values of the stabilities of the complexes of the transition elements will reflect the tendency of the cations to form dsp^2 bonds. This explanation is not, however, satisfactory in the case of the anthranilates, for magnetic susceptibility measurements suggest[7] that d levels are not involved in the bonding.

All the anthranilates* have positive values for ΔH_0, so that bonding must be weak. The order of decreasing bond strength is

$$\mathrm{Cu} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Pb} > \mathrm{Co}$$

and it is readily apparent that this is entirely different from the overall stability series. This emphasises the fact that the relative stabilities of the anthranilates cannot be discussed in terms of bond strengths only.

Previous work has not established any definite pattern in values of ΔH_0. In the few instances previously reported, with one exception[8], ΔH_0 and ΔF_0 values run parallel to each other, but in general this aspect of chelate chemistry has so far been rather neglected. If ΔH_0 values for a wide range of chelates, containing examples of different types of bonding, were determined, it might then be possible to decide which factors determine the ΔH_0 term.

The order of decreasing entropy values in the anthranilates

$$\mathrm{Co} > \mathrm{Pb} > \mathrm{Cu} > \mathrm{Cd} > \mathrm{Zn}$$

and the values range from $+64$ to -55. In the cobalt, lead and copper complexes the entropy factor appears to make a considerable contribution to the total stability.

(b) Variation of the structure of the reagent: The chelates or copper with the derivatives of anthranilic acid investigated all have low stabilities. The order of decreasing stability is

5-iodo > anthranilate > N-methyl > 5-bromo > 3:5-dibromo.

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* The values of ΔH_0 and ΔS_0 for nickel anthranilate could not be determined. Readings of the E.M.F. could only be taken at one temperature because of the tendency of nickel to absorb hydrogen.

The ΔH_0 values are all positive, so that bonding is weak throughout the series. The order of decreasing bond strength is

anthranilate > 5-iodo > 3:5-dibromo > N-methyl > 5-bromo.

Once again, the ΔF_0 and ΔH_0 series are not related.

Entropy values range from +30 to +109. The wide range, in conjunction with the wide range observed when the nature of the cation is altered, supports the view that the entropy factor is influenced both by the nature of the cation and by that of the ligand.

Finally, the relatively high stability of zinc 5-bromoanthranilate is apparently related to the bond strength, since it is the only compound with a negative ΔH_0 value. This is surprising, since the bond energies of both zinc anthranilate and of copper 5-bromoanthranilate are low. The only suggestion that can be made at this stage is that the zinc ion must react in a different fashion from the other transitional ions with a ligand containing the electronegative bromine atom, and this difference may be related to the position of zinc at the end of the transitional series. This could be tested by stability measurements on a series of chelates parallel to those described here, but with zinc replacing copper in series (ii) and 5-bromoanthranilic acid replacing anthranilic acid in series (i).

SUMMARY

The insolubility of metal anthranilates and related chelates prevents determination of their stabilities by conventional methods. A suitable electrolytic cell has been designed with which E.M.F. measurements have been made. The results obtained enable stabilities, heats of formation and entropies of formation to be derived. These are discussed in relation to the structures of the complexes.

RÉSUMÉ

L'insolubilité des anthranilates métalliques et des chélates semblables empêche la détermination de leur stabilité par les méthodes usuelles. Une cuve électrolytique appropriée est proposée, au moyen de laquelle les mesures de force électromotrice ont pu être faites. Les résultats obtenus permettent de déterminer les stabilités, les chaleurs et les entropies de formation. Une discussion est faite en relation avec les structures des complexes.

ZUSAMMENFASSUNG

Die Unlöslichkeit der Metall-Anthranilate und verwandter Chelate verhindert die Bestimmung ihrer Beständigkeit mit den üblichen Methoden. Eine geeignete elektrolytische Zelle wurde entworfen mit welcher EMK-Messungen ausgeführt wurden. Aus den erhaltenen Resultaten kann man Beständigkeiten, Bildungswärmen und Bildungsentropien ableiten. Diese werden im Verhältnis zu der Struktur der Komplexe erörtert.

REFERENCES

[1] M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 67 (1945) 2003.
[2] R. M. Keefer, *J. Am. Chem. Soc.*, 68 (1946) 2329.
[3] A. E. Martell and M. Calvin, *Chemistry of the Chelate Compounds*, Prentice Hall, New York, 1952, p. 98.
[4] *Selected Values of Chemical Thermodynamic Properties*, Circular of National Bureau of Standards, Washington, 1952.
[5] D. P. Mellor and L. L. Maley, *Nature*, 161 (1948) 436.
[6] M. Calvin and N. C. Melchin, *J. Am. Chem. Soc.*, 70 (1948) 3270.
[7] J. K. Thompson and C. L. Wilson, *Anal. Chim. Acta*, in preparation.
[8] R. G. Charles, *J. Am. Chem. Soc.*, 76 (1954) 5854.

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VARIABLE TEMPERATURE DEWAR TYPE TUBULAR DESICCATOR

by

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Familiar laboratory equipment for which the present described apparatus serves as replacement is known as a "drying pistol".

This much more efficient device is shown in the accompanying line drawing.

This Dewar style, variable heat tubular, provides a heating portion 150 mm long. The outer jacket is made of 64 mm tubing and the inner tube diameter is 48 mm. The opposite ends are closed by ₮ 50/50 male and female ground joints. The overall length of the heating mantel is 390 mm. The two stopcocks are standard taper No. 4P.

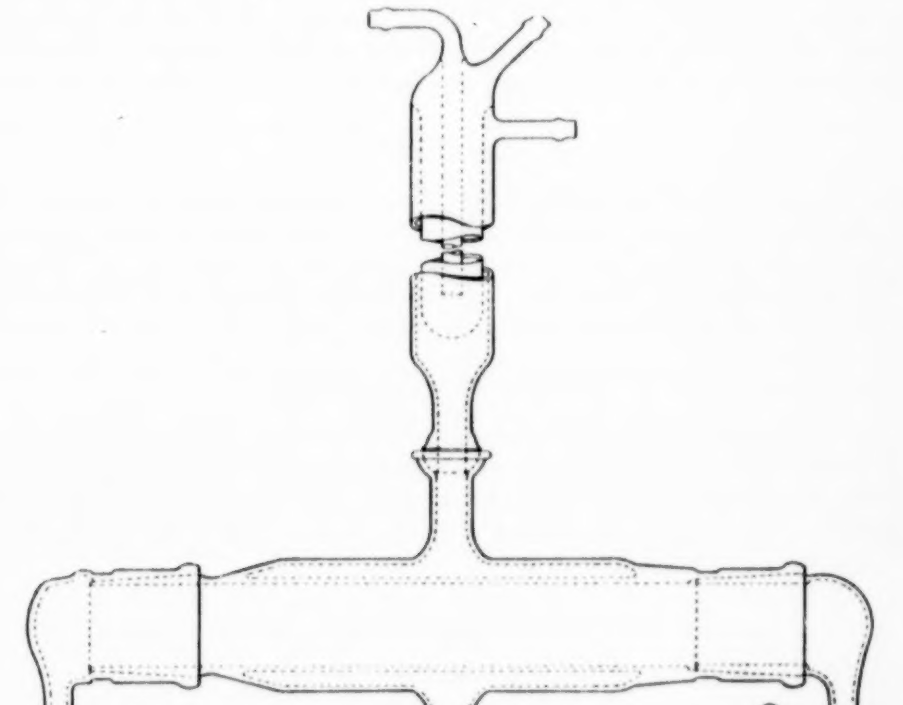

Fig. 1. "Drying pistol".

The boiler flask may be as illustrated, or, if preferred for use with an electric hot plate, may be an Erlenmeyer. The heating tube side arms are ₮ 28/15 ground ball type unions, offset 50 mm.

The condenser is 300 mm long. Alternate design reflux condenser style equipment may be substituted.

Apparatus manipulation

The device as described may be heated to selected temperatures dependent upon the type material chosen (ethanol, benzene, toluene, *n*-butanol or amyl alcohol or water), as boiler liquid.

The desiccant of highest capacity and perfect efficiency at any temperature up to 160-170°C is anhydrous magnesium perchlorate.

This desiccant is contained in a glass boat made from 42 mm tubing made into a capsule shape, 150 mm long and cut in two halves along the greater axis. Cover the boat containing the desiccant with a 50 × 150 mm section of nichrome wire gauze bent in a wide U shape to provide an overlapping side attachment to the glass boat side walls.

The material to be dehydrated or otherwise heat treated is placed in a porcelain boat which is supported by the wire gauze directly above the desiccant.

The apparatus may be attached from one end to a vacuum system. With the other stopcock closed, and boiler and return flow condenser in operation, the device duplicates the function of the less efficient "drying pistol".

An added facility is to carry out reaction procedures at ordinary pressure with aspiration of dry air through the heating chamber.

Since anhydrous magnesium perchlorate is a more efficient absorbent for ammonia gas than for water vapor, the device *in vacuo* may be employed to study the isothermal dissociation of amines and the preparation of intermediate amine types as a function of their vapor pressure at selected temperatures. The absorption of ammonia by anhydrous magnesium perchlorate to form the diammoniate is complete at temperatures under 200°C.

The reverse process may be applied, namely, the formation of amines by anhydrous metal salts such as calcium chloride, silver chloride, and the Ca, Ba, or Sr perchlorates and many other salts. In this case dry ammonia gas-air mixtures may be aspirated through the apparatus containing no desiccant or in conjunction with granular barium oxide for preliminary dehydration of the material to be tested. By this scheme the products studied need not be removed from the heating chamber. The dehydration step may be thus conducted *in vacuo* and the ammonia treatment conducted at ordinary pressure both conditions at selected variable temperatures.

For the preparation of a dry mixture of ammonia and air the following procedure is adequate and convenient:

Scrubbing towers connected in series are charged with lump ammonium carbonate, Ascarite or Mikobite, and lump barium oxide in the order given. The gas stream thus supplied, by aspiration or by slight pressure, will be anhydrous and contain several percent of ammonia.

For the supply of dry carbon dioxide gas the Ascarite or Mikobite tower and the barium oxide tower are omitted and a scrubbing tower of anhydrous magnesium perchlorate is substituted. Equilibrium studies at selected temperatures involving carbon dioxide absorption are thus provided for.

Procedure comparisons with "drying pistol" manipulations

The familiar "drying pistol" is customarily used for dehydrations under ordinary or reduced pressure and provision is not provided for selected gas aspiration.

The desiccant most often, (and unjustifiably), selected for use in the "drying pistol", is P_2O_5. This is positioned away from the heated portion of the apparatus. It is a low capacity desiccant and soon crusts over its surface upon water absorption with a moisture-impervious scum to eliminate further moisture intake.

The newly described substitute for the "drying pistol" is more versatile and of obviously higher efficiency.

If the drying pistol is still to be employed, it is still good practice to replace P_2O_5 by anhydrous magnesium perchlorate. This in the interest of actually performing well the function for which it was devised.

SUMMARY

A new designed substitute for the laboratory apparatus familiarly known as the "drying pistol" has been described and a line drawing of the new design has been provided. A discussion of manipulative details and suggestion for the numerous versatile applications possible in the use of the new equipment has been made.

RÉSUMÉ

Le schéma d'un nouveau modèle d'appareil de dessiccation est décrit, ainsi que les détails des manipulations. Plusieurs applications sont proposées.

ZUSAMMENFASSUNG

Ein neuer Trockenapparat wird beschrieben, die Einzelheiten seiner Bedienung werden erörtert und zahlreiche verschiedene Anwendungsmöglichkeiten vorgeschlagen.

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FAST GREY AS A NEW INDICATOR IN TITRATIONS WITH EDTA

by

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Complexometry has recently been the subject of a vast number of investigations. The aim of the present work is the search for a new indicator that can be applied for detecting the equivalence points in the course of titrations of a number of cations with EDTA. Such an indicator either alone or together with the already known ones may be of value in estimating a metal ion in presence of another or in estimating both in their mixture.

EXPERIMENTAL

Compounds: A number of solochrome dyes provided by the I.C.I. Company were used. The materials used either for developing colours with these dyes or as interfering elements were all of the A.R. grade. These were nitrates of Th, U, Be, Ca, Bi, Mg, chlorides of Fe, Zn, and a mixture of rare earth carbonates including La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Cp[1].

Buffer solutions: A series of buffer solutions covering the range of pH from 1 to 10[2] was used.

Determination of thorium, iron, bismuth and zinc

By preliminary tests, Fast Grey RA (1-azo-metahydroxynaphthyl-2-hydroxy-3-nitrobenzene-5-sulphonic acid) was found suitable for estimation of the above metal ions.

Determination of thorium (suitable pH 2—2.5)

Solutions

Indicator: 0.1% aqueous solution.

Thorium nitrate solution: 4.019 g of the tetrahydrate are dissolved in one liter of 0.01*N* HNO_3.

0.01*N EDTA solution:* 3.722 g are dissolved in one liter of pure H_2O.

Rare-earths solution: the calculated amount on basis of the mean atomic weight of the ions involved and their proportions is dissolved in a few ml of pure conc. HNO_3, evaporated to dryness on a water-bath and the residue then dissolved in the appropriate amount of 0.01*N* HNO_3 (1 ml = 2.5 mg rare earths).

Standardisation of the thorium solution: the thorium content was determined either as oxinate[3] or by EDTA using pyrocatechol violet indicator. As a further check the moisture content of the thorium nitrate was determined by drying a weighed sample at 100°C. The oxinate method gave a thorium content 1.4% higher though the result obtained by EDTA using pyrocatechol violet, as is seen later, is about the same as that obtained by EDTA using Fast Grey. The moisture content of 6.19% confirms the results obtained by titration.

Titrations

Different volumes of the thorium solution were titrated against 0.01 *N* EDTA solution in presence of Fast Grey (F.G.) and the results were compared with those obtained with pyrocatechol violet (P.C.V.) as shown in Table I. Microburettes of ten or five milliliter capacity were used for measuring Th and EDTA solutions.

TABLE I

Volume of Th-solution (ml)	2	4	6	8	10
End-point (F.G.)	1.36	2.74	4.095	5.44	6.83
End-point (P.C.V.)	1.365	2.73	4.075	5.42	6.80

Effect of dilution

The data in Table II are self-explanatory.

TABLE II

Constitution	*Starting vol.*	*Vol. 0.1% F.G.*	*ml Titrant vol.*
3 ml Th = 4.74 mg	3.1	0.1	2.05
3 ml Th + 50 ml 0.01 *N* HNO_3	53.2	0.2	2.049
3 ml Th + 200 ml 0.01 *N* HNO_3	203.4	0.4	2.05

starting pH : 2. Change of colour from rose red to orange occurs within 0.02 ml 0.01 *N* EDTA solution.

Effect of foreign ions

Uranium: the titration can be performed with fair accuracy in the presence of as much U^{+6} ions as 25% of the amount of Th^{+4} ions. Rare-earths (R.E.): 3 ml portions of the Th solution (4.74 mg Th) were separately titrated in the presence of increasing amounts up to 75 mg R.E. ions within a maximum error of 1%.

Other elements which are without influence are Ca, Ba, Mg, Be, and Zn. Among the interfering ions are Fe^{+3}, Bi and Zr.

Determination of thorium in the presence of iron

In the presence of microgram amounts of Fe^{+3} the titration of Th can be performed by adding one or two drops of 0.5*M* ascorbic acid to the test solution. If Fe^{+3} is present in milligram amounts, twice the amount of 0.5*M* ascorbic acid required to discharge the red colour developed with thiocyanate is added. The mixture is then heated to 68-70°C and the titration immediately performed. Thus it is possible to determine Th in the presence of equal amounts of Fe^{+3}. Results of such titrations will be mentioned later together with the ferric iron determinations.

Estimation of ferric iron

Solution : A 100 foldly diluted solution is prepared from a concentrated ferric iron solution (1 ml = 21.52 mg Fe^{+3}). The pH of the resulting solution was $\sim$ 2.

Titrations : two sets of titrations were carried out. The first set involved titrations of varying amounts of the Fe^{+3} solution with 0.01 *N* EDTA solution using F.G. as indicator, in which case the change of colour at the end-point follows from light yellow to distinct orange. The second set involved potentiometric titrations of the same volumes of the Fe^{+3} solution with 0.01 *N* EDTA solution using a recording potentiometer. Representative results of both sets of titrations are listed in Table III.

TABLE III

Volume of Fe^{+3} solution (ml)	3	6	9	10	20
End-point (F.G.)	1.163	2.325	3.484	3.87	7.735
Potentiometric end-point	1.156	2.312	—	3.858	7.705

The above data show an excellent agreement between the results obtained by the two sets of measurements with an average content of 21.59 mg Fe^{+3} per ml of the concentrated iron solution as obtained by the use of the indicator.

Effect of dilution: the results obtained by two representative titrations of 12 ml Fe^{+3} solution (2.6 mg) + 50 ml 0.01*N* HNO_3 + 0.4 ml 0.1 % F.G., and of 10 ml Fe^{+3} (2.15 mg) + 100 ml 0.01*N* HNO_3 + 0.8 ml F.G. show no deviation from the theoretical values.

Influence of foreign ions: a mixture of the cations of U, Ca, Mg, Be, and Ba in milligram amounts is of no influence, whereas in presence of such amounts of rare-earths, Bi, Th and Zn, the titration of ferric iron can not be quantitatively performed.

Analysis of mixtures of iron and thorium

Advantage is taken of the fact that the total EDTA amount required to react quantitatively with both Th^{+4} and Fe^{+3} can be determined with precision by the use of F.G. as indicator. In the presence of both cations the red colour developed by Th appears and then gradually fades, and thereafter the yellow colour of the Fe^{+3}-F.G. compound remains stable. The titration proceeds to the orange colour due to the end-point of Fe^{+3} and the amount of EDTA consumed is equivalent to that of Th + Fe. The amount of EDTA equivalent to Th alone can be determined by reduction of Fe^{+3} with ascorbic acid, heating to 68-70°C and titrating as previously mentioned. In this case the red colour due to Th remains stable and the iron no longer interferes. A similar procedure can be carried out using P.C.V. as indicator for determining Th alone after reduction of Fe^{+3} with ascorbic acid and heating to 35-40°C. Representative results of such an analysis are shown in Table IV.

TABLE IV

Titration mixture	*ml V. F.G. (Th)*	*ml V. P.C.V. (Th)*	*ml Total V. F.G. (Th + Fe)*	*ml V. (Fe)*
4.74 mg Th + 2.15 mg Fe + 0.5 ml 0.5*M* A.A.	2.05	2.052	5.92	3.868
4.74 mg Th + 4.74 mg Fe + 1 ml 0.5*M* A.A.	2.051	2.055	10.565	8.510
9.48 mg Th + 4.74 mg Fe + 1 ml 0.5*M* A.A.	4.12	4.10	12.608	8.508
7.9 mg Th + 7.99 mg Fe + 1.8 ml 0.5*M* A.A.	3.42	3.424	17.744	14.320

V = 0.01*N* EDTA solution. A.A. = ascorbic acid.

Determination of bismuth (suitable pH 2—2.5)

Bismuth solution

As is well known a solution of the nitrate $Bi(NO_3)_3 \cdot 5\,H_2O$ in dilute nitric acid when poured into a large excess of water deposits a white crystalline powder of the basic nitrate $Bi(OH)_2NO_3$. The difficulty involved in the preparation of a solution of as low acidity as pH 2—2.5 was overcome by throwing a weighed amount in boiling twice distilled water, and leaving the slightly turbid solution overnight. The solution was then filtered from the crystals deposited at the bottom of the container and used as such or after the desired dilution to the suitable pH.

Standardisation

A standard ferric iron solution (1 ml = 0.385 ml 0.01*N* EDTA solution as determined potentiometrically) was used for determining 0.005 or 0.01*N* EDTA solutions in excess of the amount required to react with different volumes of the Bi solutions, with the aid of a recording potentiometer.

Titrations

Different volumes of the bismuth nitrate solutions were titrated after addition of equal volumes of 0.01*N* HNO_3 solution against 0.002, 0.005 and 0.01*N* EDTA solutions using (F.G.) or (P.C.V.) indicators. The colour developed with F.G. indicator varied from violet to blue with increasing amount of Bi^{+3} ions. The change of colour to orange rose at the end-point occurs within 0.02 ml of the EDTA solution. Representative results are listed in Tables V, VI and VII.

TABLE V

(0.002*N* EDTA)

Bi solution (ml)	3	4	5	6	8	10
End-point by F.G. (ml)	2.475	3.337	4.13	4.936	6.60	8.25
End-point by P.C.V. (ml)	2.480	3.338	4.135	4.940	6.60	8.26

TABLE VI

(0.005*N* EDTA)

Bi solution (ml)	3	4	5	6	8	10
End-point by F.G. (ml)	2.625	3.488	4.390	5.248	7.014	8.76
End-point by P.C.V. (ml)	2.630	3.500	4.385	5.252	7.016	8.77
Potentiometric end-point (ml)	—	3.491	—	5.245	—	8.76

TABLE VII

(0.01*N* EDTA)

Bi solution (ml)	3	5	7	10	12	15
End-point by F.G. (ml)	1.852	3.052	4.33	6.16	7.39	9.25
End-point by P.C.V. (ml)	1.860	3.057	4.34	6.16	7.39	9.26
Potentiometric end-point (ml)	—	3.055	—	6.154	7.385	—

The data in the above tables indicate that F.G. can be successfully applied as indicator for direct determination of Bi with EDTA.

Effect of dilution

Experimental data indicate the reliability of the F.G. indicator for detecting the equivalence points with such low concentrations of Bi^{+3} ions as $\sim$ 30 micrograms per ml.

Influence of foreign ions

Th, Fe^{+3}, Pb and Cu interfere, whereas cations of no influence are Mg, Ca, Ba and comparatively large amounts of the previously mentioned rare-earths.

Estimation of zinc

Zinc solution : a 100 fold dilution from a zinc chloride solution (1 ml = 31.961 mg Zn as determined by the zinc pyrophosphate procedure) is used.

Buffer pH = 8 : 12.5 g NH_4Cl + 1 ml conc. ammonia are diluted to 250 ml with H_2O.

Titrations : different volumes of the Zn solution were titrated either in presence of F.G. or in presence of Eriochrome Black T, after addition of equal volumes of buffer pH = 8, against 0.01*N* EDTA solution. Volumes ranging between 6 and 40 ml of the titration mixtures required from 0.2 to 1.5 ml F.G. solution developing thereby a scarlet red colour which changed to dark violet at the end-point. Representative results are listed in Table VIII.

TABLE VIII

Zn solution (ml)	3	5	7	10	20
End-point with F.G. (ml)	1.47	2.44	3.4	4.915	9.785
End-point with E.B.T. (ml)	1.47	2.43	3.42	4.920	9.810

These data show an excellent agreement in almost all cases. They further show that 1 ml of the dilute Zn solution is equivalent to a mean value of 0.4895 ml of 0.01*N* EDTA solution corresponding to 0.31974 mg Zn per ml of the dilute solution and 31.974 mg Zn per ml of the concentrated one. The latter value shows almost no deviation from the value of 31.961 indicating the reliability of F.G. as an indicator for the direct determination of Zn with EDTA.

Effect of dilution : titrations of $\sim$2 mg Zn show that the end-points are well defined with titration mixtures not exceeding 50 ml indicating the reliability of F.G. for determining amounts of Zn as low as 40 micrograms per ml.

Influence of foreign ions

Uranium: titration of 1.6 mg Zn in presence of an equal amount of U proceeds to the theoretical end-point if U is complexed by 1 ml of 0.1 *N* $NaHCO_3$ solution.

Mg, Ca, Ba in milligram amounts are without influence, but Fe^{+3} even after reduction with ascorbic acid, Bi and rare-earths in milligram amounts should not be present.

Analysis of mixtures of Zn and Ca or Zn and Mg

Procedure: synthetic mixtures of Zn + Ca or Zn + Mg in milligram amounts were analysed by simple titration with 0.01 *N* EDTA solution using buffer pH = 8 and F.G. for determining Zn, and buffer pH = 10 and E.B.T. for determining Zn + Ca or Zn + Mg. With F.G. the colour changes from clear violet red to dark bluish violet at the end-point. The results indicate that, by aid of F.G., Zn can be determined in presence of Ca even if the amount of the latter is a little larger, and further that Ca or Mg can be indirectly determined by the above mentioned procedure.

Analysis of mixtures of Zn and Th

Synthetic mixtures of Th and Zn in milligram amounts were analysed by titrating Th with 0.01 *N* EDTA in presence of F.G. at pH = 2, in which case Zn does not show any interference. In another mixture of the same composition and after addition of buffer pH = 10 sufficient to precipitate Th and to bring the solution mixture to a pH of ∼ 10, the titration is carried out in presence of E.B.T. to the end-point of Zn where Th shows no interference. The results are in fair agreement with the previous determinations showing the reliability of the Solochromate Fast Grey RA dye as indicator for determining the above mentioned cations whether alone or in binary mixtures, with suitable EDTA solutions.

SUMMARY

An aqueous solution of the Solochromate Fast Grey RA dye has proved a suitable indicator for the direct determination of thorium, ferric iron, bismuth and zinc, or the analysis of binary mixtures: thorium-iron, zinc-calcium, zinc-magnesium or zinc-thorium, with EDTA. Thorium can be determined in presence of U, Fe, Zn, Ba, Be, Mg, and comparatively large amounts of rare earths. Ferric iron and zinc can be estimated in presence of U, Mg, Ca, Ba and Be. Cations of the rare and the alkaline earths do not interfere with the determination of bismuth.

RÉSUMÉ

Une solution aqueuse de Solochromate Fast Grey RA peut être utilisée comme indicateur pour le dosage direct du thorium, du fer(III), du bismuth et du zinc, ou pour l'analyse de mélanges binaires: thorium-fer, zinc-calcium, zinc-magnésium et zinc-thorium, au moyen de EDTA. Le thorium peut être dosé en présence de U, Fe, Zn, Ba, Be, Mg et de relativement grandes quantités de terres rares. Le fer (III)et le zinc peuvent être dosés en présence de U, Mg, Ca, Ba et Be. Les cations des terres rares et des métaux alcalino-terreux ne gènent pas le dosage du bismuth.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass eine wässrige Lösung von Solochromate Fast Grey RA ein geeigneter Indikator für die direkte Bestimmung von Thorium, Eisen(III), Wismuth und Zink oder die Analyse von binären Gemischen Thorium-Eisen, Zink-Calcium, Zink-Magnesium oder Zink-Thorium, mit EDTA. Thorium kann in Gegenwart von U, Fe, Zn, Ba, Be, Mg und verhältnismässig grossen Mengen von seltenen Erden bestimmt werden. Eisen(III) und Zink können in Gegenwart von U, Mg, Ca, Ba und Be bestimmt werden. Kationen der seltenen Erden und der Erdalkalimetalle stören die Bestimmung des Wismuth nicht.

REFERENCES

[1] F. HECHT, J. KORKISCH, R. PATZAK AND A. THIARD, *Mikrochim. Acta*, 7-8 (1956) 1283.
[2] I. M. KOLTHOFF, *Säure-Basen-Indikatoren*, J. Springer, Berlin, 1932, p. 250-258.
[3] F. HECHT AND J. KORKISCH, *Mikrochemie*, 28 (1939) 45.

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PRINCIPES DE L'IODIMÉTRIE ABSORPTIOMÉTRIQUE*

par

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INTRODUCTION

L'objet de ce travail est d'étendre l'analyse iodimétrique et iodométrique classique dans le domaine des solutions diluées. Une telle extension est possible grâce aux grands coefficients d'absorption qui caractérisent le spectre du complexe I_3^- dans l'ultraviolet proche[1,2]. L'iode analytique peut être déterminé par des mesures d'absorption lorsqu'on se place dans des conditions où il est quantitativement transformé en I_3^-. Un grand nombre d'oxydants et de réducteurs peuvent alors être dosés en mesurant tantôt une production, tantôt une consommation de I_3^-.

L'application de cette méthode d'analyse pose en général deux problèmes.

(1) Dans une solution quelconque tout l'iode ne se trouve pas à l'état de I_3^-, mais aussi à l'état de I_2 et IOH; de I_2Br^- et de I_2Cl^- en présence de chlorures et de bromures**. Quatre constantes d'équilibre caractérisent l'interaction de ces particules:

$$\begin{aligned}
K_1 &: I_3^- \rightleftharpoons I_2 + I^- \\
K_2 &: I_2 + Br^- \rightleftharpoons I_2Br^- \\
K_3 &: I_2 + Cl^- \rightleftharpoons I_2Cl^- \\
K_4 &: I_2 + H_2O \rightleftharpoons IOH + I^- + H^+
\end{aligned}$$

Ces quatre réactions atteignent l'équilibre instantanément; il suffit donc de connaître leurs constantes pour prévoir les conditions dans lesquelles l'iode analytique se trouvera quantitativement à l'état de I_3^-.

(2) L'oxydation de l'iodure par l'oxygène en milieu acide est une cause d'erreur en iodimétrie classique. Dans les conditions qui nous intéressent, cette réaction parasite peut être importante, car l'erreur relative qu'elle introduit est d'autant plus grande que les quantités d'iode à déterminer sont petites. L'application correcte de la méthode analytique exposée ici nécessite donc des renseignements quantitatifs au sujet de la cinétique de la réaction de l'iodure avec l'oxygène.

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Il fait partie de la thèse de Doctorat de J. SIGALLA, déposée à la Faculté des Sciences de l'Université Libre de Bruxelles en avril 1955 et défendue en juin 1955.

** Nous avons fait abstraction de l'existence de particules telles que IOH_2^+, IO^-, I_5^-, I_6^{-2}, I_3OH[3,4,5], dont la concentration est toujours négligeable dans les conditions susceptibles de se réaliser au cours d'une analyse.

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Au cours de cette étude, les spectres de I_2, I_3^-, I_2Br^- et I_2Cl^- ont été examinés; les constantes des équilibres auxquels participent ces particules et IOH ont été redéterminées et comparées avec les valeurs figurant dans la littérature; la cinétique de l'oxydation de l'iodure par l'oxygène dissous a été étudiée.

Ceci a permis de montrer l'existence d'un domaine étendu de conditions expérimentales, où la détermination précise d'oxydants et de réducteurs par ,,iodimétrie absorptiométrique'' est possible. La limite de détection de la méthode est de $2 \cdot 10^{-7}$ équivalent gramme d'oxydant ou de réducteur par litre lorsqu'on mesure des absorptions à travers une couche de 5 cm.

En particulier, le dosage de deux réducteurs a été mis au point: le sulfite et l'ammoniac. La détermination de l'oxygène dissous basée sur les principes de la méthode exposée ici a fait l'objet d'une communication antérieure[6].

SOMMAIRE DES RÉSULTATS DE L'ÉTUDE EXPÉRIMENTALE

1. Les spectres

Historique: dès 1907, TINKLER[7] avait étudié les spectres d'absorption de I_2, I_3^-, I_2Br^- et I_2Cl^- en solution aqueuse. L'application de ces connaissances à l'analyse quantitative ne semble pas avoir retenu l'attention: la détermination colorimétrique de l'iode par examen de ses solutions dans le tétrachlorure de carbone est encore recommandée. Par contre, CUSTER ET NATELSON[1] qui ont comparé les spectres de l'iode dans différents solvants en ont conclu que l'examen des solutions aqueuses d'iodure de potassium permet les analyses les plus sensibles. AWTREY ET CONNICK[2] ont réétudié récemment les spectres de I_2 et de I_3^-.

Réactifs et appareils: des solutions préparées à partir de produits de qualité ,,pour analyse'' et d'eau redistillée sur permanganate alcalin ont été étudiées au spectrophotomètre Beckman B, dans des cuvettes de 1 cm d'épaisseur. Un dispositif de thermostatisation a maintenu la température à 25° ± 0.1°.

Résultats: au Tableau I figurent quelques valeurs remarquables de coefficients d'extinction, au Tableau II, les points isobestiques des spectres caractéristiques de divers couples de complexes de l'iode.

TABLEAU I

COEFFICIENTS D'EXTINCTION DE I_3^- ET DE I_2 RELEVÉS AUX MAXIMA DES SPECTRES

Particule	*Auteurs*	*λ en mμ*	*Coefficient*
I_3^-	C. et N.[1]	352	$2.59 \cdot 10^4$[a]
I_3^-	A. et C.[2]	353	$2.64 \cdot 10^4$
I_3^-	nous	350	$2.51 \cdot 10^4$
I_2	A. et C.[2]	460	$7.46 \cdot 10^2$
I_2	nous	460	$6.9 \cdot 10^2$

[a] Cette grandeur a été calculée par nous, à partir des résultats de CUSTER ET NATELSON pour $[I^-] = 3.01 \cdot 10^{-1}$. Nos coefficients d'absorption sont exprimés en ion grammes par litre par cm.

TABLEAU II

POINTS ISOBESTIQUES DES SPECTRES DE DIVERS COUPLES DE COMPLEXES DE L'IODE

Couple	$I_2 - I_3^-$	$I_2 - I_2Br^-$	$I_2 - I_2Cl^-$	$I_3^- - I_2Cl^-$
λ en mμ	465	460	470	465

Nous pensons que les écarts numériques des grandeurs figurant au Tableau I sont dues aux différences d'appareillage. Soulignons que l'absorption d'une solution d'iode à 465 mμ dépend fort peu de la nature et de la quantité d'halogénure présent en solution.

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2. *Les constantes d'équilibre*

Les constantes des quatre réactions auxquelles participe l'iode sous ses différentes formes particulaires ont fait l'objet d'études nombreuses. Ces études — sauf celles de JOB[8,9] — ont porté sur des solutions d'iode plus concentrées que celles qui intéressent l'analyse absorptiométrique. Il a donc semblé utile de reprendre l'examen du problème en solution diluée. Toutes nos déterminations ont été effectuées par absorptiométrie. Les résultats sont résumés au Tableau III.

TABLEAU III

COMPARAISON DES VALEURS DES CONSTANTES D'ÉQUILIBRE TROUVÉES AU COURS DE CETTE ÉTUDE AVEC CELLES RAPPORTÉES DANS LA LITTÉRATURE

Température: 25°. I désigne la concentration analytique de l'iode.

Constante	*Fluctuations de grandeurs rapportées*	*Valeurs trouvées*	*Nos conditions*
K_1[4,10–15]	$1.30 \cdot 10^{-3}$ à $1.53 \cdot 10^{-3}$	$(1.4 \pm 0.1) \cdot 10^{-3}$	$1.52 \cdot 10^{-5} < I < 6.82 \cdot 10^{-5}$ $3.2 \cdot 10^{-4} < (I^-) < 3.2 \cdot 10^{-3}$
K_2[8,9,11,16,17]	12 à 18	15 ± 2	$I = 5.2 \cdot 10^{-4}$ $7.02 \cdot 10^{-4} < [\mathrm{Br}^-] < 5.02 \cdot 10^{-3}$
K_3[8,9,11,16,18–20]	1.5 à 2.3	1.5 ± 0.2	$I = 5.2 \cdot 10^{-4}$ $0.113 < [\mathrm{Cl}^-] < 1.58$
K_4[21,22,23–26]	10^{-11} à $5.4 \cdot 10^{-13}$	$(4.5 \pm 1) \cdot 10^{-13}$	$I = 1.04 \cdot 10^{-3}$ $7.5 \cdot 10^{-8} < [\mathrm{H}^+] < 1.75 \cdot 10^{-5}$ $6.2 \cdot 10^{-6} < [\mathrm{I}^-] < 6.7 \cdot 10^{-5}$

3. *Étude cinétique de l'oxydation de l'iodure par l'oxygène dissous**

La cinétique de la réaction de l'oxygène dissous avec l'iodure a fait l'objet d'un certain nombre de travaux. Pour des raisons qui ont été discutées[27] les conclusions de ces travaux — abstraction faite des études de la réaction d'autoxydation induite[28,29] — sont très souvent sujettes à critique. Rappelons brièvement que l'oxydation de l'iodure par l'oxygène est: 1) catalysée par les ions cuivriques et les nitrites; 2) induite en milieu neutre lors de l'oxydation de l'iodure par le pervanadyle et en milieu acide lors de son oxydation par les ions ferriques et le persulfate; 3) autocatalytique lorsque le système réactionnel est exposé à la lumière. Nous nous sommes limités à l'étude des cas suivants: a) la réaction dans l'obscurité en l'absence de catalyseur; b) la réaction dans l'obscurité, catalysée par les ions cuivriques.

a) La réaction dans l'obscurité, en l'absence de catalyseur. L'équation cinétique suivante, valable à 25°, a été établie

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{I_3}^-] = k\,[\mathrm{O_2}]\,[\mathrm{I}^-]\,[\mathrm{H}^+]$$

En solution saturée en oxygène à 25°, on a

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{I_3}^-] = 2.0 \cdot 10^{-6}\,[\mathrm{I}^-]\,[\mathrm{H}^+]$$

Dans cette équation, les concentrations sont exprimées en ion gramme par litre et le temps en minute. La constante cinétique est pratiquement indépendante de la force ionique.

b) La réaction dans l'obscurité, catalysée par les ions cuivriques. L'équation cinétique suivante, valable à 25°, a été vérifiée

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{I_3}^-] = k\,[\mathrm{O_2}]\,[\mathrm{Cu}^{+2}].\,f_1([\mathrm{I}^-]).\,f_2([\mathrm{H}^+])$$

f_1 est une fonction telle que lorsque la concentration de l'iodure croît, la vitesse augmente, passe par un maximum et puis diminue. f_2 est une fonction telle qu'à concentration croissante en ions hydrogène la vitesse augmente linéairement jusqu'à ce qu'elle se stabilise sur un palier. Pour fixer les idées, signalons qu'à concentration décimolaire en ions hydrogène et à une concentration de $3 \cdot 10^{-6}$ en ions cuivriques (concentration de ces ions dans une eau distillée usuelle), la vitesse du processus catalysé atteint le double de la vitesse du processus simple: la vitesse globale triple.

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* Ce point fera l'objet d'une publication indépendante dans laquelle le mécanisme de la réaction sera discuté.

CONCLUSIONS

L'analyse d'oxydants et de réducteurs par iodimétrie absorptiométrique est possible à deux conditions.

(a) Une condition d'équilibre: l'iode analytique doit se trouver entièrement sous forme de I_3^-. Le calcul, basé sur les constantes d'équilibre, montre que cette condition est respectée à 99% quand les 3 inégalités suivantes sont vérifiées

$$[H^+][I^-]^2 \geqslant 1.4\cdot 10^{-1}(4.5\cdot 10^{-13} + [H^+][I^-])$$
$$[I^-] \geqslant 2.1\,[Br^-]$$
$$[I^-] \geqslant 0.21\,[Cl^-]$$

Quand $[H^+] > 10^{-9}$ le premier terme du second membre de la première inégalité est négligeable et la condition se présente sous une forme plus simple

$$[I^-] \geqslant 1.4\cdot 10^{-1}$$

A pH trop élevé, un autre phénomène peut se manifester: la dismutation de l'iode en iodate et en iodure[30].

(b) Une condition cinétique: l'iode produit par autoxydation de l'iodure ne doit pas dépasser l'erreur absolue de l'analyse. Si l'on estime celle-ci à $1\cdot 10^{-7}$ mole par litre pour une détermination dans des cuvettes de 5 cm, l'équation cinétique montre que la quantité d'iode produite par la réaction parasite, dans l'obscurité et en l'absence de catalyseur, atteint l'erreur en 14 minutes, à 25°, dans une solution où $[I^-] = 0.14$ et $[H^+] = 0.1$. En général, cette équation permet de définir la concentration en ions hydrogène qu'il convient de ne pas dépasser au cours d'une détermination. En présence d'ions cuivriques, il est recommandé de réduire la concentration en ions hydrogène.

EXPOSÉ D'UN POINT PARTICULIER: LA DÉTERMINATION DE 2 CONSTANTES D'ÉQUILIBRE

1. Détermination de la constante de complexion de l'iode par les chlorures

Principe de la détermination. La détermination absorptiométrique de cette constante pose un problème: il n'est pas possible de connaître les coefficients d'extinction du complexe, car même une solution saturée en chlorures contient toujours une quantité appréciable de I_2. Nous avons procédé comme suit. Considérons deux solutions à teneur variable en chlorures et à teneur identique en iode analytique. Les chlorures sont en excès suffisant par rapport à l'iode pour que l'on puisse identifier leur concentration particulaire à leur concentration analytique. Soient I, la concentration analytique en iode, A, l'absorption à une longueur d'onde quelconque, mesurée à travers une couche de un cm d'épaisseur, r, le coefficient d'absorption de I_2Cl^-, p, celui de I_2 à la même longueur d'onde. Les six équations suivantes permettent le calcul de la constante d'équilibre.

$$[I_2Cl^-]_1 + [I_2]_1 = I$$
$$[I_2Cl^-]_2 + [I_2]_2 = I$$
$$[I_2Cl^-]_1 - K_3[Cl^-]_1\,[I_2]_1 = 0$$
$$[I_2Cl^-]_2 - K_3[Cl^-]_2\,[I_2]_2 = 0$$
$$r[I_2Cl^-]_1 + p[I_2]_1 = A_1$$
$$r[I_2Cl^-]_2 + p[I_2]_2 = A_2$$

Ce système d'équation ne contient que six inconnues: $[I_2Cl^-]_1$, $[I_2Cl^-]_2$, $[I_2]_1$, $[I_2]_2$, r et

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K_3, car p se calcule directement à partir de l'absorption d'une solution d'iode exempte d'halogénure. La solution pour K_3 est la suivante:

$$K_3 = \frac{(A_2 - p\,I)\,[\mathrm{Cl}^-]_1 - (A_1 - p\,I)\,[\mathrm{Cl}^-]_2}{[\mathrm{Cl}^-]_1\,[\mathrm{Cl}^-]_2\,(A_1 - A_2)}$$

Résultats. Préparés à partir de solutions saturées de chlorures de sodium et d'iode, les échantillons examinés ont été acidifiés par de l'acide perchlorique de manière à ce que la fraction d'iode présent à l'état de IOH soit négligeable. Les absorptions ont été mesurées au Beckman B dans des cuvettes de 1 cm thermostatisées à 25° ± 0.1°.

Les résultats sont résumés au Tableau IV et à la Fig. 1.

TABLEAU IV

ABSORPTION À 420 mμ DE SOLUTIONS D'IODE EN PRÉSENCE DE CHLORURES

$I = 5.20 \cdot 10^{-4}$; $[\mathrm{H}^+] = 7.717 \cdot 10^{-3}$

Essai no.	*1*	*2*	*3*	*4*
$[\mathrm{Cl}^-]$	1.58	0.902	0.451	0.113
A	0.430	0.390	0.345	0.270
$A-p$	0.200	0.160	0.115	0.040

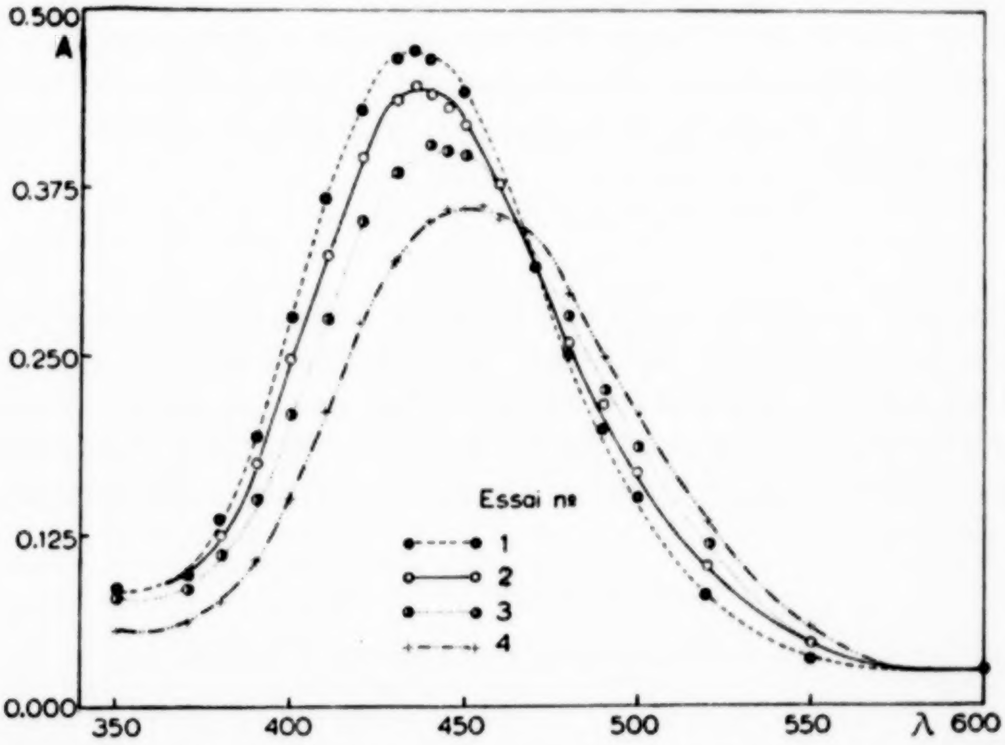

Fig. 1. Spectres d'absorption de solutions d'iode en présence de chlorures. Conditions définies au Tableau IV.

L'examen du graphique montre que les absorptions mesurées à 420 mμ se prêtent le mieux au calcul de la constante d'équilibre. p à cette longueur d'onde a été évalué indépendamment, la valeur trouvée est $4.4 \cdot 10^2$. Les constantes calculées à partir de différentes couples d'essais sont figurées au Tableau V.

TABLEAU V

CONSTANTE DE COMPLEXION DE L'IODE PAR LES CHLORURES

Couple	1—2	1—3	2—3	1—4	2—4	3—4
K_3	1.3	1.5	1.7	1.5	1.5	1.3

Conclusion: $K_3 = 1.5 \pm 0.2$

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2. *Détermination de la constante de dismutation de l'iode*

Principe de la détermination. Deux réactions se produisent simultanément dans une solution d'iode qui se dismute

$$I_2 + H_2O \rightleftharpoons IOH + I^- + H^+$$

$$I_2 + I^- \rightleftharpoons I_3^-$$

Comme les concentrations de I_2 et de I_3^- peuvent être déterminées par des mesures d'absorption à deux longueurs d'onde, on peut aussi calculer celle de l'iodure et de l'acide hypoiodeux. Les quatre concentrations se déduisent des équations suivantes

$$A_1 = p_1 [I_2] + q_1 [I_3^-] \quad \dots\dots\dots\dots \quad (1)$$

$$A_2 = p_2 [I_2] + q_2 [I_3^-] \quad \dots\dots\dots\dots \quad (2)$$

$$0 = [I^-] [I_2] - K_1 [I_3^-] \quad \dots\dots\dots\dots \quad (3)$$

$$[IOH] = [I^-] + [I_3^-] \quad \dots\dots\dots\dots \quad (4)$$

Les indices 1 et 2 se rapportent à deux longueurs d'onde. A est l'absorption, p et q les coefficients d'extinction de I_2 et de I_3^-. Ces coefficients sont connus. Les équations (1) et (2) sont valables pour des absorptions mesurées à travers une couche de un cm. La relation (4) est valable en l'absence d'iodure introduit initialement dans le système. Comme la concentration en ion hydrogène est une variable indépendante, imposée par l'expérimentateur, la constante de dismutation se calcule directement à partir de la relation qui la définit

$$K_4 = \frac{[IOH]\,[I^-]\,[H^+]}{[I_2]} \quad \dots\dots\dots\dots \quad (5)$$

Cas particulier: la solution contient initialement une trace d'iodure. L'expérience montre qu'il est très difficile de réaliser une solution d'iode exempte d'iodure. Sa concentration peut être déterminée à l'aide des équations (1), (2) et (3) si l'on se place en milieu suffisamment acide pour que l'iodure provenant de la dismutation soit négligeable. La concentration de l'acide hypoiodeux se calcule alors à partir de la relation (6) au lieu de (4)

$$[IOH] + [I^-]_i = [I^-] + [I_3^-] \quad \dots\dots\dots\dots \quad (6)$$

où $[I^-]_i$ représente la concentration de la trace initiale d'iodure.

Résultats. La procédure est analogue à la précédente. La concentration en ions hydrogène est fixée à l'aide de tampons. Les conditions choisies figurent au Tableau VI. Les spectres d'absorption correspondant sont représentés sur la Fig. 2. Les valeurs pour les essais 2 et 3, étroitement comprises entre celles de 1 et 4, elles-mêmes très proches ne s'y trouvent pas. Les grandeurs qui intéressent le calcul de la constante figurent au Tableau VII.

TABLEAU VI

CONDITIONS EXPÉRIMENTALES CHOISIES POUR L'ÉTUDE DE LA CONSTANTE DE DISMUTATION DE L'IODE

$I = 1.04 \cdot 10^{-3}$

Essai no.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
$[H^+]$	$9.024 \cdot 10^{-2}$	$7.717 \cdot 10^{-3}$	$1.18 \cdot 10^{-3}$	$1.75 \cdot 10^{-4}$	$1.75 \cdot 10^{-5}$	$1.75 \cdot 10^{-6}$	$3.75 \cdot 10^{-7}$	$7.5 \cdot 10^{-8}$
fixée par	$HClO_4$	$HClO_4$	CH_3CO_2H	CH_3CO_2H CH_3CO_2Na	CH_3CO_2H CH_3CO_2Na	CH_3CO_2H CH_3CO_2Na	KH_2PO_4 Na_2HPO_4	KH_2PO_4 Na_2HPO_4

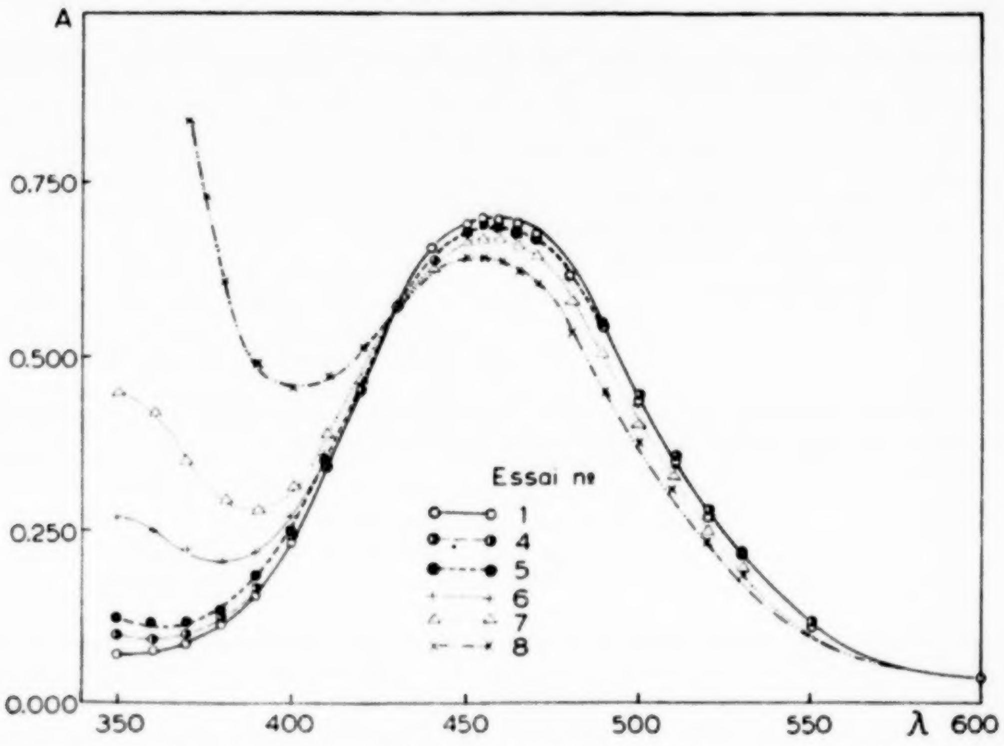

Fig. 2. Spectres d'absorption de solutions d'iode qui se dismutent. Conditions définies au Tableau VI.

TABLEAU VII

CALCUL DE LA CONSTANTE DE DISMUTATION DE L'IODE

A_1 — absorption à 350 mμ, maximum pour I_3^-
A_2 — absorption à 460 mμ, maximum pour I_2

Essai no.	*[H⁺]*	A_1	A_2	$[I_3^-]$	$[I_2]$	$[I^-]$	*[IOH]*	$K\cdot 10^{13}$	$\mu\cdot 10^{3}$
1	$9.024\cdot 10^{-2}$	0.080	0.710	$2.4\cdot 10^{-6}$	$1.04\cdot 10^{-3}$	$3.4\cdot 10^{-6}$	0	—	90
2	$7.717\cdot 10^{-3}$	0.080	0.705	$2.4\cdot 10^{-6}$	$1.04\cdot 10^{-3}$	$3.4\cdot 10^{-6}$	0	—	7.7
3	$1.18\cdot 10^{-3}$	0.085	0.700	$2.6\cdot 10^{-6}$	$1.04\cdot 10^{-3}$	$3.6\cdot 10^{-6}$	$0.4\cdot 10^{-6}$	—	1.2
4	$1.75\cdot 10^{-4}$	0.100	0.700	$3.2\cdot 10^{-6}$	$1.04\cdot 10^{-3}$	$4.5\cdot 10^{-6}$	$1.9\cdot 10^{-6}$	—	0.8
5	$1.75\cdot 10^{-5}$	0.130	0.700	$4.4\cdot 10^{-6}$	$1.04\cdot 10^{-3}$	$6.2\cdot 10^{-6}$	$4.8\cdot 10^{-6}$	5.4	8
6	$1.75\cdot 10^{-6}$	0.270	0.690	$1.0\cdot 10^{-5}$	$1.00\cdot 10^{-3}$	$1.4\cdot 10^{-5}$	$1.8\cdot 10^{-5}$	4.5	8
7	$3.75\cdot 10^{-7}$	0.455	0.665	$1.7\cdot 10^{-5}$	$9.5\cdot 10^{-4}$	$2.4\cdot 10^{-5}$	$3.5\cdot 10^{-5}$	3.2	5.6
8	$7.5\cdot 10^{-8}$	1.100	0.630	$4.3\cdot 10^{-5}$	$8.7\cdot 10^{-4}$	$6.7\cdot 10^{-5}$	$1.0\cdot 10^{-4}$	5.6	12

Remarques. (1) Nous n'avons pu réaliser une solution d'iode exempte d'iodure, sans doute à cause de la réduction de l'iode par des impuretés organiques. La concentration analytique de cette trace a été déterminée à l'aide des résultats des essais 1 et 2. On trouve $[I^-]_i = 5.8\cdot 10^{-6}$, soit 0.6% de la concentration analytique de l'iode. (2) La concentration en acide hypoiodeux étant très petite lors des essais 1, 2, 3 et 4, elle est entachée d'une grande erreur relative. Les essais ne se prêtent donc pas au calcul de la constante.

Conclusion. A 25°, à une force ionique de l'ordre de 10^{-2}, on a

$$K = (4.5 \pm 1)\cdot 10^{-13}$$

Discussion. La détermination de cette constante a fait l'objet d'un certain nombre d'études (voir Tableau III). Si la valeur 10^{-11} rapportée dans la litterature[26] diffère sensiblement de la nôtre, celle-ci concorde avec quelques déterminations récentes. Nous avons réuni au Tableau VIII quelques valeurs dont l'accord est satisfaisant.

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TABLEAU VIII

VALEURS CONCORDANTES DE LA CONSTANTE DE DISMUTATION DE L'IODE

Auteurs	$K \cdot 10^{13}$
BRAY ET CONALLY[22]	3
HORIGUCHI ET HAGISAWA[24]	4.6
ALLEN ET KEEFER[25]	5.4
Cette étude[27]	4.5

Remarque. ALLEN ET KEEFER ont déterminé la constante de dismutation par spectrophotométrie à l'aide d'une méthode analogue à la nôtre, à une date ultérieure.

RÉSUMÉ

Une méthode générale de détermination d'oxydants et de réducteurs a été étudiée. Elle est basée sur la mesure de l'absorption du spectre du complexe I_3^-. Les oxydants se déterminent par oxydation d'iodure en I_3^-, les réducteurs par réduction de I_3^-.

L'application correcte de la méthode requiert que (a) tout l'iode présent se trouve à l'état de I_3^-; (b) l'iode produit par oxydation de l'iodure par l'oxygène soit négligeable. Les constantes des principaux équilibres auxquels participe I_3^- (équilibres avec I_2, I_2Br^-, I_2Cl^-, IOH) ont été réexaminées ainsi que la cinétique de l'oxydation de l'iodure par l'oxygène en présence et en l'absence du catalyseur Cu^{+2}. Les connaissances acquises permettent de définir les conditions générales d'application de la méthode et la mise au point de dosages particuliers. La limite de détection de la méthode est de $2 \cdot 10^{-7}$ équivalent gramme d'oxydant ou de réducteur par litre lorsqu'on mesure des absorptions à travers une couche de 5 cm.

SUMMARY

A general method for the determination of oxidizing or reducing agents has been investigated. It is based on the measurement of the absorption of the spectrum of the I_3^- complex. Oxidizing agents may be determined by the oxidation of iodide into I_3^-, reducing agents by reduction of I_3^-.

For a right application of this method one must have (a) all the iodine present in the state of I_3^-; (b) the iodine produced by autoxidation of the iodide ion in negligible quantity. The constants of the chief equilibria in which I_3^- is involved (equilibrium with I_2, I_2Br^-, I_2Cl^-, IOH) and the kinetics of the autoxidation of the iodide ion in the presence and the absence of the catalyst Cu^{+2} have been reinvestigated. The acquired information enabled us to determine the general conditions of applicability of this method and the realization of special analyses. The limit of detection by this method is $2 \cdot 10^{-7}$ gram equivalent of oxidizing or reducing agent per liter when absorptions are measured through a 5 cm layer.

ZUSAMMENFASSUNG

Ein allgemeines Verfahren für die Bestimmung von Oxydations- und Reduktionsmitteln ist untersucht worden. Es gründet sich auf die Messung der Lichtabsorption des Spektrums des Komplexes I_3^-. Die Oxydationsmittel können durch Oxydation von Jodid in I_3^- bestimmt werden, die Reduktionsmittel durch Reduktion von I_3^-.

Die richtige Anwendung dieses Prozesses fordert dass (a) das ganze Jod als I_3^- anwesend sei; (b) das durch Oxydation des Jodids mit Sauerstoff produzierte Jod vernachlässigbar sei. Die Konstanten der wichtigsten Gleichgewichte an denen I_3^- beteiligt ist (Gleichgewicht mit I_2, I_2Br^-, I_2Cl^-, IOH) und die Kinetik der Autoxydation des Jodid-ions in Anwesenheit und Abwesenheit des Katalysators Cu^{+2} wurden aufs Neue untersucht. Die erworbene Kenntnis ermöglichte es die allgemeinen Bedingungen der Anwendung dieser Verfahren zu umschreiben, und auch besondere Bestimmungen auszuarbeiten. Die Empfindlichkeitsgrenze der Methode ist $2 \cdot 10^{-7}$ Gramm Äquivalent des Oxydations- oder Reduktionsmittels pro Liter wenn die Absorptionen durch eine 5 cm Schicht gemessen werden.

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BIBLIOGRAPHIE

1 J. J. CUSTER ET S. NATELSON, *Anal. Chem.*, 21 (1949) 1005.
2 A. D. AWTREY ET R. E. CONNICK, *J. Am. Chem. Soc.*, 73 (1951) 1842.
3 R. P. BELL ET E. GELLES, *J. Chem. Soc.*, (1951) 2734.
4 M. DAVIES ET E. GWYNNE, *J. Am. Chem. Soc.*, 74 (1952) 2748.
5 A. SKRABAL, *Monatsh. Chem.*, 32 (1911) 859.
6 A. BERGER, J. PIROTTE ET E. LECLERC, *Bull. Centre Belge étude et document. eaux (Liège)*, 27 (1955) 30.
7 C. K. TINKLER, *J. Chem. Soc.*, (1907) 996.
8 P. JOB, *Compt. rend.*, 182 (1926) 632.
9 P. JOB, *Ann. chim.* (Paris), [10] 9 (1928) 148.
10 A. A. JAKOWKIN, *Z. physik. Chem.*, 13 (1894) 539.
11 A. A. JAKOWKIN, *Z. physik. Chem.*, 20 (1896) 19.
12 W. C. BRAY ET G. M. J. MCKAY, *J. Am. Chem. Soc.*, 32 (1910) 915.
13 E. W. WASHBURN ET E. K. STRACHAN, *J. Am. Chem. Soc.*, 35 (1913) 691.
14 J. N. BRÖNSTED ET K. PEDERSEN, *Z. physik. Chem.*, 103 (1923) 307.
15 G. JONES ET B. B. KAPLAN, *J. Am. Chem. Soc.*, 50 (1928) 1845.
16 P. C. RAY ET D. V. SARKAR, *J. Chem. Soc.*, 121 (1921) 1449.
17 A. V. KISS ET A. URMANCZY, *Z. anorg. u. allgem. Chem.*, 202 (1931) 189.
18 S. K. RAY, *J. Indian Chem. Soc.*, 9 (1932) 284.
19 A. URMANCZY, voir GMELINS *Handbuch der anorganischen Chemie*, Leipzig-Berlin, 1926, Bnd. III, Syst. Num. 8, p. 427.
20 H. M. DAWSON ET E. SPIVEY, *J. Chem. Soc.*, (1932) 1840.
21 W. C. BRAY, *J. Am. Chem. Soc.*, 82 (1910) 932.
22 W. C. BRAY ET E. L. CONALLY, *J. Am. Chem. Soc.*, 33 (1911) 1485.
23 E. ANGELESCU ET V. D. POPESCU, *Z. physik. Chem.*, A 156 (1931) 304.
24 G. HORIGUCHI ET H. HAGISAWA, voir W. M. LATIMER, *Oxidation Potentials*, 2nd Edition, Prentice Hall, New York, 1953, p. 64.
25 T. L. ALLEN ET R. M. KEEFER, *J. Am. Chem. Soc.*, 77 (1955) 2957.
26 G. CHARLOT, *Théorie et Méthode Nouvelle d'Analyse Qualitative*, Masson, Paris, 1946, p. 235.
27 J. SIGALLA, *Thèse*, Bruxelles, 1955.
28 W. C. BRAY ET J. B. RAMSEY, *J. Am. Chem. Soc.*, 55 (1933) 2279.
29 J. B. RAMSEY ET M. H. BOYER, *J. Am. Chem. Soc.*, 75 (1953) 3802.
30 A. SRABAL, *Z. Elektrochem.*, 40 (1934) 243.

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SÉPARATION ET DOSAGE DE TRACES DE BORE DANS LE SILICIUM*

I. APPLICATION DE LA MÉTHODE D'EXTRACTION CHLOROFORMIQUE SOUS FORME DE FLUOBORATE DE TÉTRAPHÉNYLARSONIUM

par

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Nous avons tenté de doser le bore contenu à l'état de traces dans du silicium en appliquant le procédé décrit par COURSIER, HURÉ ET PLATZER[1]: extraction chloroformique sous forme de fluoborate de tétraphénylarsonium (TAS)***, puis dosage à la curcumine selon PHILIPSON[2].

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* Ces deux mémoires ont fait l'objet de communications au XVième Congrès de Chimie Pure et Appliquée (Lisbonne, Septembre 1956).

** Avec la collaboration technique de B. GARCIA ET L. PATEAU.

*** Pour abréger, nous dirons toujours par la suite TAS au lieu de tétraphénylarsonium.

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Au cours de ce travail, diverses difficultés se sont présentées et nous avons été amenés à préciser ou à modifier sur plusieurs points ces méthodes. Nous commencerons par indiquer le mode opératoire adopté à la suite d'essais très nombreux. Nous en soulignerons ensuite les points les plus importants dans des notes explicatives en donnant quelques détails sur les raisons pour lesquelles nous insistons sur certaines recommandations. Nous avons dû nous borner à présenter beaucoup de celles-ci sous une forme purement empirique faute de pouvoir entreprendre les études détaillées qui eussent été nécessaires pour les justifier scientifiquement. Nous discuterons enfin des moyens d'augmenter la sensibilité de la méthode et nous suggérons des variantes évitant l'emploi du chlorure de TAS, réactif rare et coûteux.

MODE OPÉRATOIRE

Attaque du silicium et mise en solution du bore sous forme d'ions BF_4^-

Dans 6 flacons de forme identique comprise entre 60 et 125 ml, en polyéthylène de bonne qualité, numérotés et soigneusement bouchés, on attaque six fois:

50 mg de silicium finement pulvérisé dans un mortier d'agate ou d'alumine et passé au tamis 200, d'abord par: 5 gouttes d'une solution aqueuse à 0.2% de chlorure de cuivre(II), puis par 1 ml d'une solution 20*M* (densité 1.19) d'acide fluorhydrique pur pour analyses, 2 ml d'une solution 7.5*M* (427.5 g/l) de bifluorure d'ammonium ($FNH_4 \cdot FH$) pur pour analyses, 1 ml de perhydrol pur à 30% de H_2O_2.

Pour que l'attaque soit bien complète et suffisamment rapide, on a intérêt à chauffer doucement les flacons (maintenus bien bouchés) vers 40—50°, par exemple, en les posant sur l'étuve qui sert à la cuisson de la curcumine.

Au début de l'opération ou après la fin de l'attaque, on ajoute dans les flacons no. 3 et 4, 0.5 ml et dans les flacons no. 5 et 6, 1 ml d'une solution titrée d'acide borique contenant 0.5 mg de bore par litre, soit donc respectivement 0.25 et 0.50 μg. Après la fin de l'attaque, on ajoute dans chaque flacon 12 ml d'eau, on rebouche soigneusement les flacons et on les laisse reposer pendant 18 heures au moins.

Extraction du fluoborate de TAS

On transvase le contenu des six flacons d'attaque dans autant de flacons identiques qui ne servent qu'à des extractions.

On ajoute dans chaque flacon 15 ml d'une solution chloroformique à 4 g/l (approximativement *M*/100) de chlorure de TAS. On bouche soigneusement les six flacons et on les agite tous ensemble pendant une demi-heure sur une machine à secouer. On a avantage à accélérer ensuite la séparation des couches aqueuse et chloroformique par centrifugation. On élimine la couche aqueuse en l'aspirant à l'aide d'une pissette souple en polyéthylène.

On verse alors dans chaque flacon 10 ml d'eau qu'on décante aussitôt de la même façon, sans avoir agité.

Cette opération, que nous appelons ,,prélavage'', est suivie de deux lavages proprement dits. On effectue chacun de ceux-ci en agitant énergiquement à la main pendant 30 secondes les six flacons simultanément, après avoir versé 15 ml d'eau dans chacun d'eux et les avoir soigneusement bouchés. On élimine ensuite la couche aqueuse comme il vient d'être indiqué. On a en général également avantage à centrifuger avant de décanter.

On transvase ensuite les solutions chloroformiques dans autant de capsules identiques en platine, de forme basse ordinaire, à bec, de taille 30 ml, numérotées. On ajoute dans chaque capsule à l'aide d'une pipette graduée en polyéthylène ou en quartz 0.75 ml de solution d'hydroxyde de sodium *N*/10 préparée et conservée dans un flacon en polyéthylène.

On amène à sec le contenu des six capsules simultanément sous rayonnement infra-rouge.

Préparation, contrôle et conservation de la solution de curcumine

Préparation : On utilise pour le dosage du bore une solution de curcumine préparée de la manière suivante:

On traite, au voisinage de 0°, 315 mg de curcumine pure cristallisée par 30 ml d'alcool éthylique. On filtre rapidement sur verre fritté no. 4 et on étend la solution à 250 ml avec le même alcool.

Essai préliminaire : On doit immédiatement contrôler la solution ainsi obtenue par l'essai suivant que nous appellerons ,,essai préliminaire'':

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Dans chacune des six capsules en platine, on met 0.75 ml d'hydroxyde de sodium $N/10$ puis, dans les capsules no. 3 et 4 d'une part, 5 et 6 d'autre part, respectivement 0.5 et 1.0 ml d'une solution titrée d'acide borique contenant 0.5 mg/l de bore. On amène les six capsules à sec sous rayonnement infra-rouge et on effectue le dosage à la curcumine comme il est indiqué plus loin.

Portés sur un graphique en fonction de la quantité de bore ajoutée, les six résultats de la colorimétrie doivent être bien groupés deux par deux au voisinage d'une même droite avec des écarts ne dépassant pas 0.01 unité de densité optique (sous réserve d'un écart accidentel par excès provenant de l'introduction d'une trace de bore par les poussières de l'air).

L'expérience a montré de plus, sans que nous ayons pu trouver de justification à ce résultat empirique, que si la pente de la droite ne correspond pas à 1.28 ± 0.02 unité de densité optique par μg de bore, il vaut mieux ne pas poursuivre les opérations et préparer une nouvelle solution de curcumine, sous peine d'obtenir des résultats peu cohérents.

Essai à blanc : Si l'essai préliminaire est satisfaisant, on procède à un essai à blanc en effectuant toute la suite des opérations indiquées ci-dessus avec cette seule différence qu'on n'attaque pas de silicium, puis le dosage à la curcumine comme il est indiqué plus loin.

L'expérience a montré qu'on n'est assuré d'obtenir des dosages pleinement satisfaisants que si, dans cet essai à blanc, les six résultats de la colorimétrie, portés sur un graphique en fonction de la quantité de bore ajoutée, sont bien groupés deux par deux, au voisinage d'une droite dont la pente correspond à 1.02 ± 0.02 unité de densité optique par μg de bore avec des écarts ne dépassant pas 0.01 unité de densité optique (avec la même tolérance d'un écart accidentel par excès).

Conservation : Même si elle donne satisfaction à l'essai préliminaire et à l'essai à blanc, la solution de curcumine s'altère lentement, surtout sous l'action de la chaleur, de la lumière et de l'air. Il faut donc la conserver en flacon bouché de préférence en verre coloré et au froid. Même ainsi, on ne peut espérer la conserver beaucoup plus de 3 à 4 semaines et il convient de refaire de temps à autre l'essai préliminaire pour juger de son évolution.

Dosage à la curcumine

Dans chaque capsule de platine amenée à sec comme il est indiqué plus haut, on met: 1 ml de la solution de curcumine dont on vient de décrire la préparation et le contrôle, 1 ml d'alcool, un volume V de solution aqueuse molécluaire d'acide trichloracétique, déterminé dans des essais préalables de façon à répondre à la condition empirique suivante: au bout de 55 minutes de chauffage dans l'étuve utilisée, réglée entre 105 et 106°, le contenu des capsules doit être encore liquide. Au bout de 60 minutes il doit être sec et cristallisé en belles aiguilles. Avec l'étuve que nous utilisons actuellement au laboratoire, $V = 1.3$ ml.

Les six capsules ainsi préparées sont placées dans une étuve dont la température est réglée avec le plus grand soin entre 105 et 106°. Au bout de 60 minutes on vérifie que le contenu des capsules est sec et bien cristallisé. S'il est encore humide, on peut éventuellement prolonger un peu la cuisson, mais sans dépasser 65 à 70 minutes.

On retire alors les capsules de l'étuve. On en reprend le contenu par de l'alcool et on ajuste à 20 ml le volume des solutions ainsi obtenues, dans autant de fioles jaugées numérotées. On effectue alors la colorimétrie de ces solutions à la longueur d'onde de 5400 Å, dans une cuve en verre, d'épaisseur 2 cm.

Portés sur un graphique comme il est indiqué plus haut les six réultats de l'opération de dosage doivent être groupés deux par deux au voisinage d'une droite de même pente que celle donnée par l'essai à blanc, avec des écarts ne dépassant pas 0.01 unité de densité optique (toujours sous réserve d'un écart accidentel par excès).

Dépouillement des résultats

Soient respectivement a et b, les densités optiques correspondant aux ordonnées à l'origine des droites autour desquelles sont groupés respectivement les résultats de l'essai à blanc et ceux du dosage lui-même, portés sur un graphique en fonction des quantités de bore ajoutées. Soit p la pente commune de ces deux droites (ou la moyenne de leurs pentes) exprimée en unités de densité optique par μg de bore. (On a vu qu'en principe $p = 1.02 \pm 0.02$.) La teneur en bore d'un échantillon est $\frac{b-a}{p}$. Comme la masse d'un échantillon est de 50 mg, la concentration en bore du silicium étudié est:

$$10^{-6}\,\frac{20\,(b-a)}{p} \text{ soit environ } 20\,(b-a)\,10^{-6}.$$

Précision des mesures

Dans les cas les plus favorables, a et b sont déterminés à 0.005 unité de densité optique près, donc $(b-a)$ à 0.01 unité près. La teneur en bore est donc connue à $2\cdot10^{-7}$ près. En fait, cette précision est rarement atteinte et ne dépasse souvent pas $5\cdot10^{-7}$.

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NOTES EXPLICATIVES

Flacons en polyéthylène

Une grande partie des difficultés que nous avons rencontrées avait son origine dans le polyéthylène des flacons. Il n'est pas rare que celui-ci contienne une proportion notable de produits extractibles par le chloroforme, qui perturbent le dosage par la curcumine. Il est recommandé, avant de mettre un flacon en service, de vérifier qu'il ne présente aucune odeur et de le faire tremper pendant au moins 24 heures dans du trichloréthylène, puis, quand on ne l'utilise pas, de le maintenir plein d'eau pour éviter l'oxydation lente par l'air. Lors de l'attaque, le polyéthylène est oxydé mais les produits formés, insolubles dans les solutions aqueuses, ne sont pas gênants du fait qu'on transvase les liqueurs dans une autre série de flacons pour l'extraction chloroformique.

Attaque du silicium

L'eau oxygénée seule ne suffit pas comme oxydant. Il faut lui adjoindre un catalyseur. Le chlorure de cuivre s'est montré extrêmement efficace. (Il est à noter que le sulfate de cuivre n'a pas donné toute satisfaction.)

Toutefois, on ne peut l'employer qu'avec certaines précautions: les essais ont montré en effet que, ni le chlorure de cuivre ni l'eau oxygénée, pris isolément ne gênent la suite des opérations. Mais dès que l'eau oxygénée, est en présence d'ions cuivriques dont la concentration n'est pas extrêmement faible, elle oxyde la solution de chlorure de TAS ajoutée par la suite, en donnant des produits qui perturbent fortement le dosage par la curcumine. De plus, les ions cuivriques paraissent catalyser l'oxydation du polyéthylène des flacons, tant par l'eau oxygénée que même par l'oxygène de l'air. La meilleure manière d'éviter ces inconvénients est, d'une part, comme il a été indiqué de disposer de deux séries différentes de flacons pour l'attaque et l'extraction, et d'autre part de n'employer qu'une quantité de chlorure de cuivre aussi faible que possible. D'où le mode opératoire préconisé: on n'utilise qu'une solution déjà étendue de chlorure de cuivre (0.2%) et en quantité juste suffisante pour mouiller le silicium finement pulvérisé. Le cuivre se dépose sur ce dernier en formant des couples locaux qui favorisent sa mise en solution. Le cuivre ne se redissout qu'à la fin de l'attaque et se trouve porté par le volume total de la solution (16 à 18 ml), à une concentration trop faible pour être nuisible.

On évite de plus ainsi un autre inconvénient: en présence de trop de sel cuivrique, l'attaque est brutale; une partie de l'eau oxygénée se décompose en dégageant de l'oxygène gazeux qui risque d'entraîner une partie de bore.

D'autres oxydants ont été essayés avec succès: permanganate de potassium, chlore, brome. On en détruit l'excès par un peu de bisulfite. Les variantes de la méthode ont l'inconvénient d'augmenter fortement le volume des solutions aqueuses. Ni l'iode, ni l'acide nitrique ne conviennent en raison de leur action, même à l'état de traces sur la curcumine.

Composition et concentration du milieu pour l'attaque du silicium, puis la formation des ions BF_4^-

L'excès d'acide fluorhydrique au départ a été calculé de façon à donner un pH final acceptable (compris entre 2.5 et 3) et à permettre l'utilisation des mêmes quantités de réactifs pour des attaques portant sur 100 mg de silicium. La dilution finale par de l'eau est indispensable car nous avons constaté, comme COURSIER, HURÉ ET PLATZER[1] que la formation des ions BF_4^- est moins complète en solution très concentrée en acide fluorhydrique.

Cependant nous arrivons à une concentration totale en fluorure plus élevée (2.5*M*) que celle qu'adoptent ces auteurs (0.8*M*); et s'en approcherait davantage (1.8*M*) dans le cas de l'attaque de 100 mg de silicium.

Eau : Dans toutes ces opérations il convient de n'utiliser que de l'eau pratiquement exempte de bore (eau redistillée dans un appareil à double effet en quartz et recueillie dans des récipients en polyéthylène ou en quartz).

Repos : Cette condition est extrêmement importante car l'équilibre n'est atteint que lentement.

Chlorure de TAS

Il convient de vérifier avec soin la pureté de ce produit. Certains produits commerciaux contiennent en effet des impuretés organiques qui donnent à la solution une teinte jaune et perturbent la suite des opérations, et parfois des quantités relativement importantes de bore, qui donnent des valeurs très élevées lors de l'essai à blanc.

Dans les deux cas, il faut purifier le produit par recristallisation ou mieux extraction.

Centrifugation : On peut utiliser pour cette opération des tubes en polyamide.

Décantation : Cette opération est un peu délicate et exige un certain tour de main.

Lavages : Le prélavage a pour but d'éliminer les dernières traces de réactif d'attaque qui ont pu rester sur les parois des flacons; les lavages proprement dits, d'éliminer l'excès de chlorure de TAS[1] qui nuit au dosage par la curcumine en provoquant la formation de laques.

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Curcumine

Tous les auteurs s'accordent à déplorer l'extrême difficulté et l'irrégularité des dosages à la curcumine. Nous avons déjà indiqué l'influence néfaste de certaines impuretés. Nous préciserons dans les notes suivantes l'effet de quelques autres facteurs, mais sans prétendre avoir élucidé toutes les causes d'échec.

Il faut souligner le fait que la curcumine commerciale semble ne pas avoir des propriétés parfaitement définies et que, même à l'état solide, elle s'altère à l'air, à la lumière et à la chaleur.

Il semble qu'une simple dissolution complète de la curcumine commerciale donne en général des résultats plus irréguliers que le mode de préparation indiqué.

Sensibilité de l'essai préliminaire

Très souvent on observe une pente moyenne supérieure à 1.28, en général de l'ordre de 1.40, mais pouvant atteindre 1.80. Les résultats restent alors bien groupés deux par deux, mais s'alignent mal sur une droite. De plus, l'essai préliminaire n'est alors pas reproductible avec une bonne précision.

Une telle curcumine permet seulement de se faire une idée de la teneur en bore si celle-ci est relativement importante (de l'ordre de quelques 10^{-5}).

Les solutions bonnes au moment de leur préparation, vieillissent au bout de 2 à 3 semaines, même conservées au froid et à l'obscurité. Cela se traduit par une baisse des pentes moyennes et de la sensibilité des dosages.

Il est préférable que dans l'essai préliminaire l'ordonnée à l'origine de la droite corresponde à une densité optique faible, de l'ordre de 0.10 à 0.15.

Sensibilité de l'essai à blanc

Le fait d'obtenir une pente de 1.28 à l'essai préliminaire est une condition nécessaire, mais non toujours suffisante, pour que l'essai à blanc donne des résultats bien groupés au voisinage d'une droite de pente 1.02. Mais si cette dernière condition est aussi remplie, on est à peu près certain que les dosages seront corrects.

Choix de l'étuve, réglage de la température

M. COURSIER nous avait signalé le choix de l'étuve et son réglage comme extrêmement délicats et d'une importance fondamentale. Notre expérience nous a confirmé l'exactitude de ces indications.

Si la température dépasse 106°, le contenu des capsules brunit et la sensibilité de la réaction diminue très rapidement jusqu'à rendre tout dosage impossible. Si l'enceinte demeure trop longtemps au-dessous de 105°, la réaction est incomplète; les couleurs obtenues sont instables et s'évanouissent même parfois pendant la durée de la mesure.

Si on emploie une étuve à gaz, il ne faut pas que les gaz de combustion puissent pénétrer dans l'enceinte.

Dilution finale

Le contenu doit se dissoudre très rapidement et totalement dans l'alcool (il ne nous a pas paru utile que celui-ci contienne une trace d'acide trichloracétique comme le recommande PHILIPSON[2]. Ce n'est en général pas le cas s'il n'est pas bien cristallisé en belles aiguilles.

Normalement les solutions ont une couleur rose stable qui persiste sans affaiblissement notable pendant une dizaine d'heures.

POSSIBILITÉ D'AMÉLIORER LA SENSIBILITÉ DES DOSAGES

En raison de la dispersion habituelle des résultats, on ne peut guère espérer en améliorer beaucoup la précision. Mais il est surtout intéressant d'en augmenter la sensibilité pour l'étude des siliciums très pauvres en bore. Un gain pourrait être réalisé en pratiquant la colorimétrie dans des cuves plus épaisses et sur des solutions moins diluées, mais il paraît difficile d'utiliser moins de 10 ml par capsule. Un progrès plus important serait obtenu en attaquant de plus gros échantillons de silicium. Au-delà de 100 mg, il faudrait modifier les quantités indiquées de réactifs. Nous estimons cependant qu'on ne saurait dépasser 500 mg du fait de l'augmentation des volumes des solutions et de la teneur en bore non négligeable des produits commerciaux les plus purs, en particulier le bifluorure d'ammonium.

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VARIANTES POSSIBLES DE LA MÉTHODE

En raison de la rareté et du manque de pureté trop fréquent du chlorure de TAS commercial, nous avons cherché à extraire le bore sous forme d'un fluoborate autre que celui de TAS.

Des essais préliminaires nous ont montré la possibilité d'utiliser le chlorure du duodécylpyridinium, dont le fluoborate est extractible par l'acétate de butyle, et le chlorure de triméthylstéarylammonium, dont le fluoborate est extractible par le chloroforme ou le dichloréthane. Malheureusement, dans les deux cas, le solvant organique extrait aussi un gros excès du chlorure, dont il est ensuite difficile de se débarrasser sans perdre de bore, et qui gêne pour le dosage à la curcumine.

Nous n'avons pas poursuivi ces essais en raison des succès obtenus par l'un d'entre nous dans une autre voie : extraction du bore sous forme de fluoborate d'une base colorée (*o*-phénanthroline ferreuse ou bleu de méthylène) et dosage direct par colorimétrie dans le solvant organique d'extraction. Cette méthode est plus simple, plus précise et présente l'immense avantage d'éviter tout recours à la curcumine.

RÉSUMÉ

On décrit, avec de nombreux détails opératoires, l'application au cas du silicium de l'extraction de traces de bore sous forme de fluoborate de tétraphénylarsonium, selon la méthode de COURSIER, HURÉ ET PLATZER, et du dosage de ces traces par la curcumine selon la méthode de PHILIPSON, et on donne quelques brèves indications sur d'autres méthodes de séparation et de dosage de traces de bore.

SUMMARY

A description is given, together with numerous operative details, of the application to the case of silicon of the extraction of traces of boron in the form of tetraphenyl-arsonium fluoroborate, according to the COURSIER, HURÉ AND PLATZER method, and of the estimation of these traces by curcumin, according to the PHILIPSON method. Some brief information is given about other methods for the separation and determination of traces of boron.

ZUSAMMENFASSUNG

Die Anwendung der Extraktion von Spuren von Bor als Tetraphenylarsoniumfluoroborat nach der Methode von COURSIER, HURÉ UND PLATZER, und der Bestimmung dieser Spuren mit Kurkumin nach der Methode von PHILIPSON, auf den Fall des Siliciums, wurde mit zahlreichen Einzelheiten des Arbeitsganges beschrieben.

Einige kurze Anleitungen für andere Methoden zur Abtrennung und Bestimmung von Spuren von Bor werden gegeben.

BIBLIOGRAPHIE

1 J. COURSIER, J. HURÉ ET R. PLATZER, *Anal. Chim. Acta*, 13 (1955) 379.
2 T. PHILIPSON, *Lantbruks-Högskol. Ann.*, 12 (1944-1945) 251.

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SÉPARATION ET DOSAGE DE TRACES DE BORE DANS LE SILICIUM

II. NOUVELLE MÉTHODE DE SÉPARATION ET DE DOSAGE DE TRACES DE BORE. APPLICATION AU DOSAGE DU BORE DANS LE SILICIUM

par

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PRINCIPE DE LA MÉTHODE

Dans le mémoire précédent nous avons exposé les difficultés que présente le dosage de traces de bore par la curcumine, en particulier après séparation par extraction chloroformique du fluoborate de tétraphényl-arsonium[1]. J'ai cherché un dosage plus simple et plus rapide présentant une sensibilité au moins égale à celle de la curcumine en m'appuyant sur le principe suivant: utiliser un borate ou un fluoborate très coloré, si possible peu soluble dans l'eau, mais soluble donc extractible par un solvant organique convenablement choisi. Après extraction on pourra effectuer directement le dosage par spectrocolorimétrie après étalonnage.

Pour rechercher un fluoborate très coloré insoluble dans l'eau, j'ai utilisé l'analogie chimique existant entre les fluoborates (BF_4^-) et les perchlorates (ClO_4^-). Les propriétés des perchlorates en solution étant en général mieux connues que celles des fluoborates, ce sont les premiers qui m'ont guidé au cours de cette étude: on sait par exemple que l'orthophénanthroline ferreuse utilisée couramment comme indicateur d'oxydo-réduction, donne avec l'ion perchlorique un composé insoluble dans l'eau. L'ion fluoborique donne également avec ce cation complexe: $[(o\text{-ph})_3Fe]^{+2}$ un précipité rouge peu soluble dans l'eau. On cherche alors à dissoudre ce composé dans l'un des solvants usuels ou dans un liquide organique couramment rencontré au laboratoire. Sont étudiés à cet effet les hydrocarbures aliphatiques, aromatiques et leurs dérivés halogénés, les premiers termes des alcools, aldéhydes, cétones, esters . . .

On trouve ici que les cétones aromatiques, et en particulier l'acétophénone, sont des solvants utilisables. En effet le fluoborate d'*o*-phénanthroline ferreuse se dissout assez facilement dans l'acétophénone en donnant au liquide une coloration rouge intense. Mais ce solvant dissout l'acide fluorhydrique. Or, la présence de cet acide à une forte concentration est nécessaire à la formation de l'ion fluoborique en solution aqueuse[1]. Au cours de l'extraction, une partie de l'acide passe dans la phase organique, et l'utilisation des cuves de verre ou de quartz pour les mesures colorimétriques devient alors impossible. On peut neutraliser l'acide par une base organique (en ajoutant une solution alcoolique de pyridine par exemple) mais on diminue la sensiblité qui est déjà très inférieure à celle de la curcumine: à 1 μg de bore ajouté à la solution aqueuse correspond après extraction par 15 ml d'acétophénone, une densité optique voisine de 0.05 (cuve de 2 cm).

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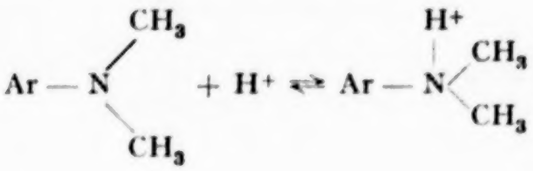
L'*a,a'*-dipyridyl ferreux donne également un précipité rouge peu soluble dans l'eau, extractible par une cétone aromatique, mais la sensibilité est encore inférieure à la précédente.

Parmi les réactifs proposés pour caractériser les perchlorates figure le bleu de méthylène. En effet ce produit se classe dans le groupe des colorants basiques; la molécule renferme une fonction amine substituée et en milieu suffisamment acide il se forme le cation correspondant suivant le schéma : $M + H^+ \rightleftharpoons MH^+$ en désignant par M la molécule de bleu de méthylène ou encore:



Ce cation très coloré, donne un précipité avec l'ion perchlorique. L'ion fluoborique donne également avec ce cation un précipité bleu-violacé que j'ai utilisé finalement pour la séparation et le dosage des traces de bore.

Recherche du solvant: Parmi les nombreux liquides organiques étudiés seul le 1,2-dichloréthane est un solvant pratiquement utilisable. Les autres solvants chlorés aliphatiques étudiés: chloroforme, tétrachlorure de carbone, trichloréthylène, 1,2-dichloréthylène ne dissolvent pas le précipité.

Les dérivés halogénés aromatiques comme: monochlorobenzène, monobromobenzène, dichlorobenzène le dissolvent faiblement.

Le 1,2-dichloréthane présente de plus la propriété indispensable de ne pas dissoudre la forme moléculaire du bleu de méthylène.

ÉTUDE DES DIFFÉRENTS FACTEURS DE L'EXTRACTION ET DU DOSAGE DU BORE

pH d'extraction. Influence de l'extraction de fluorhydrate de bleu de méthylène

L'anion fluoborique ne se forme et n'existe que dans certaines conditions qui ont été systématiquement étudiées[2]: en milieu acide, par exemple en tampon fluorhydrique, c'est-à-dire à un pH voisin de 3.2. Le pH d'extraction est donc pratiquement fixé à cette valeur qui est compatible avec l'existence du cation organique. En effet, le bleu de méthylène étant une base faible, le cation correspondant n'existe qu'en milieu très acide.

Ecrivons que le fluoborate extrait par la phase organique est en équilibre avec ses ions en phase aqueuse:

$$\underset{\text{Dichloréthane}}{(BF_4MH)} \rightleftharpoons BF_4^- + MH^+$$

Soit K la constante de cet équilibre:

$$\frac{[BF_4^-]\,[MH^+]}{[BF_4MH]} = K$$

c_0 la concentration initiale du fluoborate dans la phase aqueuse et c sa concentration en phase organique après extraction, il vient en supposant que les volumes des deux phases sont égaux et en écrivant le bilan du bore: $c_0 = c + [BF_4^-]$:

$$c_0 = c\left(1 + \frac{K}{[MH^+]}\right)$$

Si la concentration du cation MH^+ est suffisamment grande, sa variation au cours de l'extraction est négligeable et cette relation montre que la quantité de fluoborate extrait (c) est proportionnelle à la concentration initiale c_0. On peut donc utiliser cette extraction même si elle n'est pas quantitative, pour doser les traces de bore. Ici, cependant le phénomène est plus complexe. En effet, dans les conditions opératoires imposées pour la formation de l'ion fluoborique, la concentration des ions F^- en phase aqueuse est grande (0.5 par exemple). Dans ces conditions le dichloréthane extrait du fluorhydrate de bleu de méthylène bien que le coefficient de partage apparent soit très faible. L'expérience montre que le coefficient d'extraction du fluoborate est fonction de la concentration du fluorhydrate dans la phase organique. Lorsque cette concentration augmente (addition de fluorhydrate à la phase aqueuse par exemple), le rendement de l'extraction du fluoborate diminue.

Les concentrations des ions F^- et MH^+ doivent être choisies en fonction de ces remarques, mais la concentration de F^- doit être suffisamment élevée pour que se forme l'anion fluoborique. Cette concentration étant fixée on détermine pour chaque dosage la concentration optimum du bleu de méthylène.

D'autre part, on peut prévoir qu'il sera indispensable de se placer dans des conditions d'extraction identiques si l'on veut obtenir des résultats reproductibles et proportionnels aux quantités du bore à doser.

Des extractions successives effectuées à 20° montrent que le rendement de l'extraction du fluoborate est compris entre 80 et 85%, en employant le mode opératoire décrit plus loin.

Comme il est dit précédemment, après extraction la phase organique est très colorée, car elle renferme outre la majorité du fluoborate, du fluorhydrate de bleu de méthylène. Il est donc nécessaire de procéder après élimination de la couche aqueuse, à un lavage de la phase organique par de l'eau pour éliminer le fluorhydrate de bleu de méthylène.

Au cours de cette opération, une très faible quantité de fluoborate passe dans la solution de lavage. En effet, c'est le fluorhydrate de bleu de méthylène qui passe presque quantitativement dans l'eau, qui renferme alors des ions F^- et MH^+. La présence de ces ions dans la phase aqueuse limite le déplacement vers la droite de l'équilibre:

$$\underset{\text{Dichloréthane}}{(BF_4MH)} \rightleftharpoons BF_4^- + MH^+$$

Temps d'extraction: L'équilibre est atteint très rapidement, une agitation de quelques minutes suffit.

Ions gênants: Les cations Al^{+3}, Fe^{+3}, Be^{+2}, Si^{+4} ne gênent pas.

Certains anions sont extractibles dans les mêmes conditions par le dichloréthane: ClO_4^-, SCN^-, $Cl_3C{\cdot}CO_2^-$ quantitativement, MnO_4^-, NO_3^- partiellement.

Influence de la température

De faibles variations de température (20° ± 5°) n'ont aucune influence sur le rendement de l'extraction. Cependant les résultats ne sont bien reproductibles que si la température est constante et identique pour toutes les analyses, pendant la formation de l'ion fluoborique qui demande au moins 18 heures[1,2]. En effet, l'expérience montre que la quantité d'ion fluoborique formé dépend de la température; elle diminue lorsque la température augmente.

Influence de la pureté du solvant

Le 1,2-dichloréthane commercial renferme en général d'autres produits chlorés en quantité variable suivant les origines.

Ces différences de composition entraînent de faibles variations du rendement de l'extraction et perturbent les dosages précis. Il est donc recommandé de rectifier le produit commercial et de ne conserver pour l'extraction que la fraction passant à température constante (83° ± 1°). Eviter également la présence de traces de matières grasses.

Spectrocolorimétrie

Le spectre d'absorption du fluoborate de bleu de méthylène dans le dichloréthane présente un maximum à 6450 Å. En utilisant cette longueur d'onde, la loi de Lambert-Beer est parfaitement suivie.

APPLICATIONS

A. Dosage de traces de bore dans l'eau

Mode opératoire pour 10 ml de solution

Réactifs (note 1)

Solution de bifluorure d'ammonium $7.5M$ (note 2).
Solution d'acide borique à 0.5 μg de bore par ml.
Solution de bleu de méthylène $2 \cdot 10^{-2}M$ (note 3).
1,2-Dichloréthane rectifié.

Matériel

Matériel de laboratoire (flacons, pipettes, etc.) en polyéthylène pour la manipulation des solutions fluorhydriques.
Microburettes (en verre ordinaire).
Flacons de polyéthylène (note 4; voir 1)

Prendre 6 flacons de polyéthylène numérotés de 1 à 6. Dans chaque flacon placer 10 ml de la solution à analyser; puis dans les flacons 1 et 2 ajouter 1 ml (microburette) d'eau distillée sur quartz, dans les flacons 3 et 4, 0.5 ml d'eau et 0.5 ml de la solution d'acide borique (soit 0.25 μg), dans les flacons 5 et 6, 1 ml de la solution d'acide borique (soit 0.50 μg). Ajouter ensuite dans chaque flacon 1 ml de la solution de bifluorure, boucher les flacons et les abandonner au moins 18 heures à température constante. Ajouter ensuite dans chaque flacon 3 ml de solution de bleu de méthylène et 15 ml de dichloréthane. Agiter mécaniquement 5 minutes, centrifuger (ou laisser décanter), puis retirer avec soin à l'aide d'une pissette de polyéthylène la couche aqueuse. Ajouter ensuite 10 ml d'eau bidistillée, agiter mécaniquement 1 minute, centrifuger (ou laisser décanter). Eliminer la couche aqueuse comme précédemment et effectuer la colorimétrie.

Les résultats doivent être groupés deux à deux et se placer sur une droite, si l'on porte sur un graphique les densités optiques en ordonnées et les quantités de bore ajoutées en abscisses. La pente de cette droite donne la sensibilité de la méthode.

Un ,,essai à blanc'' effectué dans les mêmes conditions en remplaçant la solution à analyser par de l'eau bidistillée, permet de doser le bore apporté par les réactifs. On obtient donc par différence la teneur en bore de la solution à analyser.

Sensibilité de la méthode et précision des mesures. En utilisant pour les mesures des cuves de 2 cm, 1 μg de bore correspond à une densité optique voisine de l'unité. (Pour un mode opératoire donné c'est une fonction de la température de formation de l'ion fluoborique.)

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Quelle que soit la quantité de bore dosé l'erreur maximum absolue sur une détermination pour un manipulateur entraîné, varie entre 0.005 et 0.01 unité de densité optique, soit environ 0.005 à 0.01 μg.

B. Dosage de traces de bore dans le silicium

Attaque du silicium. Les attaques classiques par la soude ou le mélange d'acide nitrique et d'acide fluorhydrique présentent ici des inconvénients:

La soude commerciale ,,pour analyse'' renferme en général trop de bore pour être utilisée dans une méthode de dosage aussi sensible.

L'attaque nitro-fluorhydrique donne une solution acide qu'il faut ensuite neutraliser en partie par une base. De plus les ions NO_3^- en excès sont extractibles partiellement.

J'ai adopté le mode d'attaque décrit dans le mémoire précédent: oxydation en tampon fluorhydrique par l'eau oxygénée en présence de chlorure cuivrique.

La réaction s'écrit:

$$Si + 4\,HF + 2\,F^- + 2\,H_2O_2 \rightleftharpoons [Si\,F_6]^{-2} + 4\,H_2O$$

Mode opératoire pour 100 mg de silicium

Le silicium doit être broyé finement. Pour cette opération l'emploi d'un mortier au carbure de tungstène est recommandé. On peut utiliser également un mortier d'agate; il est facile de vérifier que l'agate ne s'use pas suffisamment pour apporter du bore en quantité dosable.

Réactifs

Solution fluorhydrique: préparée par addition d'acide fluorhydrique à du bifluorure d'ammonium (note 2).

concentrations HF: 10N.
F^-: 7.5N.

Solution de chlorure de cuivre(II) à 5%.
Eau oxygénée ,,électro'' 110 volumes.
Solution de bleu de méthylène $10^{-2}M$ (note 3).
Solution d'acide borique à 0.5 μg de bore par ml.
Dichloréthane rectifié.

Matériel

Voir le mode opératoire précédent et la note 4.

Placer dans 6 flacons de polyéthylène numérotés de 1 à 6 : 100 mg de silicium finement broyé. Ajouter ensuite dans chaque flacon les réactifs comme il est indiqué dans le Tableau I.

TABLEAU I

Flacons	*Solution de bore ml*	*Eau bidistillée ml*	*Solution fluorhydrique ml*	*H_2O_2 ml*
1	0	5	2	1
2	0	5	2	1
3	0.5	4.5	2	1
4	0.5	4.5	2	1
5	1	4	2	1
6	1	4	2	1

Ajouter ensuite 1 goutte de chlorure cuivrique. Boucher les flacons. L'attaque du silicium demande environ 20 minutes. Abandonner au moins 18 heures à température constante. Ensuite ajouter dans chaque flacon 3 ml d'eau bidistillée 5 ml de solution de bleu de méthylène et 15 ml de dichloréthane. Poursuivre l'analyse comme précédemment.

,,Essai à blanc'': Détermination du bore contenu dans les réactifs: cet essai doit s'effectuer exactement dans les mêmes conditions que le dosage, c'est-à-dire en présence de concentrations iden-

tiques de FH, F^-, SiF_6^{-2} etc. . . ., ce qui suppose la présence en solution d'un silicium sans bore ou d'un silicium de titre connu.

Si l'on ne possède pas de silicium étalon, on peut opérer de la manière suivante à condition de disposer d'un échantillon assez pur dont la teneur est approximativement connue, comprise par exemple entre 10^{-7} et $5 \cdot 10^{-7}$; le principe utilisé est le suivant: la formation de BF_4^- étant très lente (18 heures au moins), si l'on effectue l'extraction immédiatement après l'attaque du silicium, seul le bore des réactifs est extrait, à condition de préparer le mélange des réactifs 20 heures avant l'attaque. On peut vérifier que si l'opération dure au total environ une demi-heure, moins de 5% du bore du silicium utilisé passe dans la phase organique, ce qui est négligeable devant les erreurs d'expérience.

Si l'on ne possède que du silicium à teneur élevée (10^{-6} à 10^{-5} par exemple) cette méthode ne peut donner qu'une valeur approchée par excès de l'essai à blanc, mais permet cependant de découvrir parmi les échantillons de silicium proposés à l'analyse des échantillons plus purs qui permettront alors une meilleure détermination.

Mode opératoire

On prépare comme indiqué dans le Tableau II les mélanges que l'on abandonne au moins 18 heures.

TABLEAU II

Flacons	*Solution de bore ml*	*Eau bidistillée ml*	*Solution fluorhydrique ml*	*H_2O_2 ml*
1	0	8	2	1
2	0	8	2	1
3	0.5	7.5	2	1
4	0.5	7.5	2	1
5	1	7	2	1
6	1	7	2	1

Après cette attente, on verse ces mélanges sur 100 mg de silicium préalablement pesé dans une autre série de flacons et sur lequel on a ajouté 1 goutte de chlorure de cuivre(II).

Immédiatement après attaque (tiédir si nécessaire) ajouter 5 ml de solution de bleu de méthylène, 15 ml de dichloréthane et continuer comme précédemment.

Exemple: Température 20° ± 1°.

Le silicium utilisé pour l'étalonnage (essai à blanc) renferme environ $2 \cdot 10^{-7}$ de bore. Il a été traité comme il vient d'être indiqué.

TABLEAU III

	Essai à blanc			*Silicium inconnu*		
Flacons	*Densité optique en centième d'unité*	*Moyenne*	*Différence*	*Densité optique en centième d'unité*	*Moyenne*	*Différence*
1	33.3	33.2		36.3	36.5	
2	33.1		23.1	36.7		23
3	56.1	56.3		59.6	59.5	
4	56.5		23	59.4		23.2
5	79.6	79.3		82.4	82.7	
6	79			83		

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Ces résultats montrent que 1 μg de bore correspond ici à une densité optique voisine de 0.92.

La différence d'ordonnées entre les deux droites est en moyenne de 3.3 centième d'unité. Le silicium analysé renferme $(3 \pm 0.5) \cdot 10^{-7}$ de bore.

C. Dosage dans la silice

On peut décrire un mode opératoire pour la silice en supprimant l'eau oxygénée et le chlorure cuivrique; mais le mode opératoire précédent peut s'appliquer en remplaçant 100 mg de silicium par 214 mg de silice, ce qui évite un nouvel étalonnage lorsque celui-ci a déjà été effectué pour le dosage du bore dans le silicium.

NOTES

Note 1

Les solutions aqueuses seront préparées si possible avec de l'eau bidistillée dans un appareil en quartz.

Note 2

Parmi les réactifs utilisés, c'est le bifluorure d'ammonium qui est en général le plus riche en bore. Employer de préférence le produit livré dans des flacons en matière plastique.

Note 3

Utiliser de préférence le bleu de méthylène „médicinal". En utilisant un produit impur, il peut arriver que l'extraction du fluoborate soit pratiquement nulle ou d'un rendement très faible. Ajouter alors à la solution de bleu de méthylène filtrée sur verre fritté No. 4, quelques gouttes de chlorure de cuivre(II) à 0.5%, et faire barboter de l'air pendant une douzaine d'heures. Filtrer de nouveau.

Note 4

L'eau oxygénée, en présence de chlorure de cuivre(II) oxyde le polyéthylène de mauvaise qualité en donnant des acides gras, dont les sels de cuivre colorés sont extractibles par le dichloréthane ce qui perturbe le dosage. Il est préférable de posséder deux séries de flacons:

l'une utilisée pour l'attaque du silicium et la formation du fluoborate
l'autre réservée à l'extraction.

RÉSUMÉ

On décrit une nouvelle méthode de séparation et de dosage de traces de bore par extraction du fluoborate de bleu de méthylène par le dichloréthane. La méthode est appliquée au dosage de traces de bore dans le silicium et la silice.

SUMMARY

A new method is described for the separation and determination of traces of boron by extraction of methylene blue fluoroborate by dichlorethane. The method has been applied to the determination of traces of boron in silicon and silica.

ZUSAMMENFASSUNG

Eine neue Methode zur Abscheidung und Bestimmung von Spuren von Bor durch Extraktion des Methylenblau-Fluoroborates mit Dichloräthan wird beschrieben. Die Methode wird zur Bestimmung von Bor-Spuren in Silicium und Siliciumdioxyd angewendet.

BIBLIOGRAPHIE

L. DUCRET ET P. SEGUIN, *Anal. Chim. Acta*, 17 (1957) 207.
J. COURSIER, J. HURÉ ET R. PLATZER, *Anal. Chim. Acta*, 13 (1955) 379.

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THE MICRO VOLUMETRIC DETERMINATION OF URANIUM WITH APPLICATION TO BISMUTH BASE ALLOY ANALYSIS

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INTRODUCTION

The volumetric determination of uranium on a macro and semi micro scale by reduction to the tetravalent state with a lead reductor followed by titration against ceric sulphate is now a well established procedure[1,2]. The need arose for a method for the determination of small amounts of uranium in bismuth base alloys. These alloys were expected to contain small amounts of zirconium, calcium and iron in addition to from 0.005 to 0.1% of uranium. The determination of such small amounts of uranium required either an extension of the volumetric method to the microgram level of uranium or, alternatively, the application of absorptiometric or polarographic procedures. Various considerations including that of adequate sensitivity at the lowest concentrations of uranium favoured the volumetric method with the consequent development of the micro lead reductor described in this paper. Unfortunately, this reductor method could not be applied directly in the presence of bismuth and iron, and separation procedures proved necessary for the determination of uranium in bismuth base alloys.

EXPERIMENTAL

Construction and use of the micro lead reductor

A scaled down version of the macro reductor was found suitable for the determination of small amounts of uranium. It was made from a 10 cm length of glass tubing of 3 mm internal diameter and with a capacity of about 0.3 ml. To assist the transfer of solutions to the reductor, a small filter funnel of about 3 ml capacity was fixed to the top of the tube by a polythene sleeve. A small glass ball of approximately 2 mm in diameter supported the column of granulated lead (40-60 mesh) which almost filled the reductor. The flow of liquid from the lower tip could be stopped when necessary by pushing on a piece of small bore soft rubber tube suitably closed at the lower end. A plug of this type proved necessary to prevent air being forced into the reductor in the process of stopping the flow of liquid. Full details of the reductor are given in Fig. 1.

The reductor was prepared from good grade granulated lead (40-60 mesh) kept under 10% v/v hydrochloric acid. Sufficient of this material was taken and stirred to break down any aggregates of the lead particles. At the same time the reductor column and funnel was filled with 10% v/v hydrochloric acid and examined to ensure the complete absence of air bubbles. The lead was next transferred to the column with the aid of a stream of 10% v/v hydrochloric acid from a wash bottle, whilst allowing some of the acid to run out of the reductor. The lead was allowed to aggregate by gently tapping the column and then the acid was drained down to the top of the funnel stem. If the lead did not present a bright metallic surface, it was necessary to treat the column with concentrated hydrochloric acid. This can be achieved by placing the end of the reductor in a beaker of concentrated hydrochloric acid and then applying suction to the other end to suck the acid up through the column. By adding 10% v/v hydrochloric acid to the beaker and continuing the suction procedure, the weaker acid can be re-introduced into the reductor column without the introduction of air. It is important to maintain the level of acid above the lead in the funnel stem and for efficient working it is generally necessary to repack the column each day.

Uranium is reduced by the passage of a solution of the material in 2 ml or less of 10% v/v hydrochloric acid through the reductor, followed by 1 ml of this acid to wash the reductor. This solution is collected in a 5 ml tall-form micro beaker. The uranium is then titrated with standard ceric sulphate which is added from an Agla syringe burette fitted with a micrometer screw. The tip of the burette is stationary and immersed beneath the liquid in the beaker. The beaker on the other hand is secured by adhesive to a horizontal platform which can be rotated by an air-driven stirrer and by this means thorough mixing of the solution is obtained during the titration procedure. The solution is made approximately normal in sulphuric acid before the uranium is titrated against ceric sulphate either directly in the presence of 0.02 ml of phosphoric acid (sp.gr 1.75) using ferroin as the indicator or indirectly after the addition of ferric alum, the ferrous iron produced being titrated in this case again with ferroin as the indicator. The ferrous iron in the ferroin also consumes ceric sulphate and therefore the amount of indicator used must be carefully measured. The indicator blank constitutes the major part of the titration blank, since the blank on the column is small and tends to disappear with use of the column. The 0.04 ml of $0.001N$ ferroin recommended for most titrations produces a blank titre of 0.8 μl of $0.05N$ ceric sulphate which is equivalent to 4.8 μg of uranium.

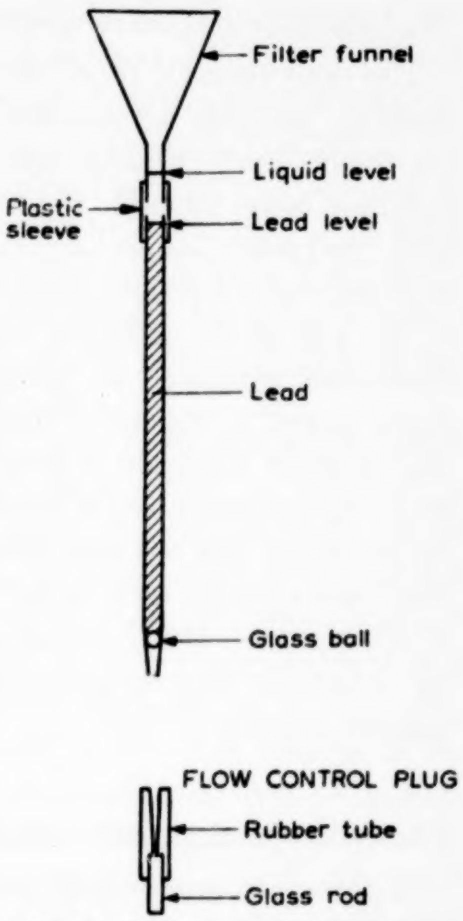

Fig. 1. The micro lead reductor

Determination of uranium

The complete procedure for the determination of microgram amounts was tested on suitable aliquots of a standard solution of uranium in 10% v/v hydrochloric acid. This solution was prepared from pure U_3O_8 by treating it with a small amount of perchloric acid and heating to effect the solution of the oxide. This solution was diluted with 10% v/v hydrochloric acid so as to contain 1 mg of uranium per ml of solution, that is 1 μg per microlitre. Suitable aliquots were dispensed from a second Agla microburette and passed down the micro reductor after mixing with 2 ml or less of 10% v/v hydrochloric acid. Various amounts of uranium in the range from 1-500 μg were determined by the complete method using both the direct and the indirect titration procedures. The results are given in Table I from which it can be seen that good recoveries were obtained at all levels. The titrations were carried out with different strengths of ceric sulphate in the range from 0.01 to $0.05N$ and with amounts of ferroin indicator varying from 0.02 ml of $0.00025N$ to 0.04 ml of $0.001N$, depending on the amount of uranium present. The accuracy of the determination was studied in some detail at the 7 μg level of uranium. Several determinations were carried out by different operators using $0.01N$ ceric sulphate and 0.02 ml of $0.001N$ ferroin. Under these conditions the coefficient of variation was 1% and the uranium recovery was low by 1%. The use of $0.05N$ ceric sulphate and 0.04 ml of $0.001N$ ferroin is recommended in the titration procedure as being suitable for most purposes.

TABLE I

TYPICAL RESULTS FOR THE RECOVERY OF URANIUM BY THE MICRO LEAD REDUCTOR

1. Direct titration procedure									
Uranium taken,	μg	1.0	6.0	11.9	20.0	50.0	100	250	500
Uranium recovered,	μg	0.9	6.2	11.8	19.9	50.0	101	247	497
2. Indirect titration procedure									
Uranium taken,	μg	50.0	100	250	500				
Uranium recovered,	μg	50.0	101	249	498				

The behaviour of other elements in the uranium determination

The behaviour of other elements was not examined very thoroughly in this investigation, because information is available for many elements from the studies with the macro lead reductor and those substances causing interference with the macro reductor could be expected to cause difficulty on the micro scale. In this work, therefore, the behaviour of only those elements present in the alloy samples was checked. Bismuth caused serious difficulties because it is reduced to the metal forming a deposit at the top of the reductor and thereby gradually blocks the column. In the case of zirconium, although it caused no difficulty in the reduction process, troubles were encountered in the direct titration due to the precipitation of zirconium phosphate. The indirect titration still applied, however, and the colour change from brown to green at the end-point was readily detected. Under these conditions a ten fold excess of zirconium did not interfere in the uranium determination. In the case of thorium there was no difficulty in the direct titration procedure even for a hundred fold excess of this element. However, on the basis of information from the macro reductor method for uranium, interferences to be avoided are chiefly iron, nitrate (and nitrite) and organic matter.

The determination of the uranium content of bismuth base alloys

A procedure was required for the determination of the uranium content of bismuth base alloys containing from 50 to 1000 p.p.m. of uranium, 200-300 p.p.m. of both calcium and zirconium and small amounts of contaminating iron. In view of the unfavourable behaviour of bismuth with the lead reductor, the preliminary removal of the bismuth from the uranium was absolutely essential. The separation of iron from uranium was also necessary before the lead reductor method for uranium could be applied. This latter separation can be readily effected by an anion exchange procedure reported by ARNFELT[3]. In this method a sulphate solution of the sample is adjusted to pH 2 and the iron is then reduced to the ferrous state. On passing this solution through a small column of Deacidite FF in the sulphate form, the uranium is retained on the column whereas many other elements including iron are not retained. The uranium can then be subsequently recovered from the column in dilute hydrochloric acid (10% v/v) and its concentration determined volumetrically after the destruction of organic matter present in solution from the ion-exchange column. Unfortunately, this separation procedure cannot be applied simultaneously to the removal of bismuth, since bismuth is not in solution at pH 2 and would cause blockage of the ion exchange column.

Several methods are available for the separation of bismuth from uranium and consideration was given to most of them. An ion exchange process involving the passage of a solution of the sample in *N* hydrochloric acid through a column of Deacidite FF in the chloride form is one possible procedure[4]. However, it was finally concluded that a method involving two ion-exchange separations would be too time consuming for routine analysis. A possible single ion exchange process to effect the separation of the bismuth and iron on one column was next examined. This consisted of passing the sample solution in 4*N* hydrochloric acid down a column of Deacidite FF in the chloride form after the addition of stannous chloride to the solution to reduce iron to the ferrous state. Under these conditions the uranium is retained on the column with bismuth and tin, whereas the reduced iron passes through. The uranium can then be recovered by the passage of dilute hydrochloric acid through the column and the determination completed volumetrically. This procedure proved unsatisfactory in practice, however, because of difficulty in avoiding pick up of iron inherent in the large resin columns when carrying out the hydrochloric acid procedure. According to BURSTALL AND WELLS[5] the separation of uranium from bismuth and iron is possible by cellulose column chromatography, bismuth and iron being retained on the column whilst the uranium passes through in the ether-nitric acid eluant. Experiments soon showed however that although this technique was satisfactory with amounts of bismuth of about 100 mg, it was not suitable for larger samples.

Another method for the separation of bismuth is based on the fairly low boiling point of bismuth bromide. On evaporating a bismuth solution down to dryness in the presence of a mixture of bromine and hydrobromic acid, the bismuth can be volatilised from the beaker. It is generally necessary to heat the walls of the beaker with a bunsen flame to remove any condensed bismuth from them. On repeating this evaporation process with several separate portions of the bromine-hydrobromic acid mixture, it is possible to remove quite readily amounts of bismuth up to 1000 mg. This separation method was applied to this problem and it fitted in well with the subsequent ion-exchange process for the separation of uranium from iron. The final residue from the evaporation procedure was simply dissolved in 2-3 drops of concentrated sulphuric acid and this solution was diluted to a volume of 25 ml. After the adjustment of the pH to a value of 2, the iron was reduced to the ferrous state with sulphur dioxide and the ion-exchange separation of the uranium then carried out. Full details of the complete procedure for the analysis of alloy samples are as follows:

Procedure for the determination of uranium in bismuth alloys

Weigh out 1 g of the alloy, dissolve in 50% v/v nitric acid in a 100 ml beaker and then evaporate to dryness. Add about 2 ml of a bromine solution containing 85% v/v of hydrobromic acid, 15% v/v of bromine and 0.2 g of potassium bromide per 100 ml. Place the beaker in an efficient fume hood and evaporate to dryness. Gently flame the beaker with a bunsen and continue heating to drive off the bismuth. When the evaporation ceases, cool the beaker and add a further 2-3 ml portion of the bromine mixture. Again evaporate to dryness on a hot plate and repeat the fuming procedure. Repeat the process four or five times to ensure the removal of the bismuth. Cool the beaker after the last evaporation, add 2-3 drops of concentrated sulphuric acid to dissolve the residue and dilute the solution with water to a volume of about 25 ml. Adjust the pH of this solution to a value of 2 by the addition of ammonium hydroxide. Then add a few crystals of *o*-phenanthroline and 2 ml of a saturated solution of sulphur dioxide in water. Warm the solution on a hot plate to effect the reduction of the iron, the intensity of the colour of the solution becoming constant when the reduction reaches completion. Cool and reserve for the ion-exchange separation.

Make a 2 ml column of Deacidite FF resin of 40-60 mesh (see Fig. 2). Prepare the resin by grinding some of the commercial resin ($-16 + 50$ mesh) in the chloride form and sieving the material to obtain that which passes through a 40 mesh sieve. Wash the resin in a large column with dilute sulphuric acid until the effluent contains a negligible quantity of chloride. Prepare a smaller column from this material and pass the sample solution down it at the rate of 1 drop every 5 seconds. Then wash the column with a few ml of very dilute sulphuric acid adjusted to pH 2. Place a 50 ml volumetric flask under the column, elute the uranium with about 40 ml of 10% v/v hydrochloric acid and make the solution up to volume. Take a convenient aliquot of this solution and evaporate it to dryness in a small clean platinum dish. Carefully drive off the small amount of sulphuric acid which will be present and then heat over a flame to oxidise any organic matter carried down from the resin column. Add 2 drops of sulphuric acid (sp.gr. 1.84) and heat to fumes to dissolve the U_3O_8. Allow the warm sulphuric acid to run over the inside of the dish to effect complete solution of the uranium. Rinse this solution into the micro lead reductor using < 2 ml of 10% v/v hydrochloric acid. Wash the platinum dish with a further 1 ml of 10% v/v hydrochloric acid and pass down the reductor. To the reduced solution from the column, add 0.04 ml of 0.001 N ferroin and 1 drop of a 20% w/v solution of ferric alum in 5% v/v sulphuric acid. Titrate the uranium which should be $\sim N$ in H_2SO_4

with a standard 0.05N ceric sulphate solution and calculate the results from the fact that 1 μl of 0.05N ceric sulphate is equivalent to 5.95 μg of uranium. Carry out a blank determination on the complete procedure. Also, always test the lead reductor with known amounts of uranium before reducing any sample solutions. A satisfactory uranium standard solution is made by dissolving 1.179 g of U_3O_8 in an initial 20 ml of perchloric acid with heating. This solution is diluted to 1 l using 10% HCl. 1 μl = 1 μg U.

RESULTS AND CONCLUSIONS

The complete procedure has been tested on synthetic alloy samples prepared from bismuth metal of better than 99.99% purity. The other constituents were of Specpure or AnalaR quality and 100 p.p.m. of iron was included in each sample. The satisfactory results for uranium by this procedure are given in Table II. These results take into account blank determinations carried out on synthetic samples containing no uranium. The full blank generally amounted to a uranium equivalent of about 15 μg, approximately one quarter of this, however, arising from the indicator blank alone.

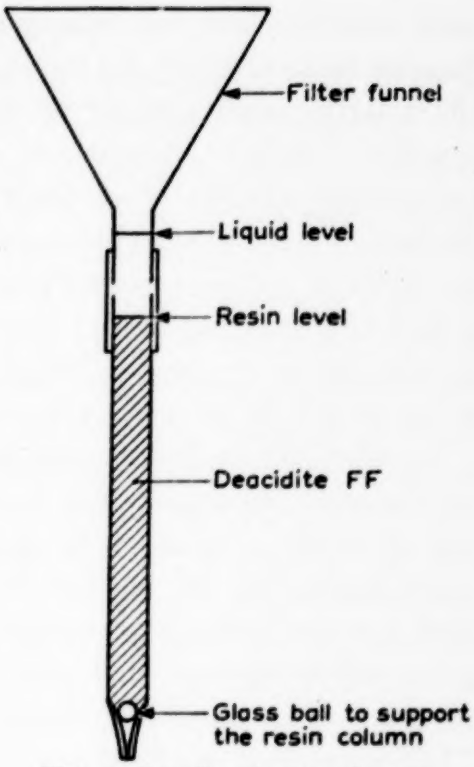

Fig. 2. Small anion-exchange column.

TABLE II

ANALYSIS OF SYNTHETIC BISMUTH BASE ALLOYS

Weight of uranium μg	*Uranium* %	*Weight of uranium in alloy by analysis* μg	*Uranium in alloy by analysis* %	*Error in uranium determination* %
1000	0.100	984	0.098	−2
1000	0.100	1007	0.101	+1
400	0.040	392	0.039	−2.5
400	0.040	405	0.041	+2.5
50	0.005	47	0.0047	−6
50	0.005	52	0.0052	+4

SUMMARY

The macro volumetric method for the determination of uranium by titration against standard ceric sulphate after reduction on a lead column has been successfully applied on the micro scale. Microgram amounts of uranium can be determined by this method, the lowest amount determinable being about 1 microgram. The procedure is accurate to within ± 1% at the 100 μg level of uranium. Although bismuth and iron cause difficulty, there is no interference from zirconium or thorium.

This method for uranium has been applied to the analysis of bismuth base alloys containing uranium in concentrations from 0.005 to 0.1% by weight.

RÉSUMÉ

La methode volumétrique pour le dosage de l'uranium, par titrage au moyen d'une solution étalon de sulfate de cérium après réduction sur une colonne de plomb, a été appliquée avec succès à des dosages microchimiques. Des traces d'uranium peuvent être dosées par cette méthode, la plus petite quantité titrable étant d'environ 1 μg. Ce dosage est précis: ± 1% pour 100 μg d'uranium. Le bismuth et le fer gênent, ce qui n'est pas le cas du zirconium ou du thorium. Cette méthode a pu être appliquée à l'analyse des alliages à base de bismuth renfermant 0.005 à 0.1% d'uranium.

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ZUSAMMENFASSUNG

Die makrovolumetrische Methode zur Bestimmung von Uran durch Titrieren mit einer Standard-Cersulfat-Lösung nach Reduktion auf einer Bleisäule wurde mit Erfolg für Mikromengen angewendet. Mikrogramm-Mengen an Uran können mit Hilfe dieser Methode bestimmt werden, wobei die niedrigste bestimmbare Menge ungefähr 1 Mikrogramm ist. Das Verfahren ist genau innerhalb ± 1% bei Gehalten von der Grössenordnung 100 µg Uran. Obwohl Wismuth und Eisen Schwierigkeiten bereiten, stören Zirkonium und Thorium nicht. Diese Methode wurde zur Analyse von Legierungen auf Wismuthbasis, welche Uran in Konzentrationen von 0.005 bis 0.1 Gewichtsprozent enthalten, angewendet.

REFERENCES

[1] C. W. SILL AND H. E. PETERSON, *Anal. Chem.*, 24 (1952) 1175.

[2] A. BACON AND G. W. C. MILNER, *Atomic Energy Research Establishment*, Report C/R 1813, H. M. Stationery Office, 1956.

[3] A. L. ARNFELT, *Acta Chem. Scand.*, 9 (1955) 1484.

[4] G. W. C. MILNER AND J. W. EDWARDS, *Atomic Energy Research Establishment*, Report C/R 2143 (1956), to be published.

[5] F. H. BURSTALL AND R. A. WELLS, *Analyst*, 76 (1951) 396.

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QUANTITATIVE ESTIMATION OF HALOGENATED ORGANIC ACIDS ON PAPER CHROMATOGRAMS

by

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A simple and accurate method is described for the quantitative estimation of halogenated organic acids on paper chromatograms. Bromo- and iodo-acids could be estimated accurately ≥ 98% by this method. The procedure for the qualitative separation of these acids on paper chromatograms was described in a previous paper[1].

EXPERIMENTAL

Materials

Propanol was purified by distillation. The concentrated ammonia was A.R. grade (s.g. 0.088). 0.1% solution of eosin and 1% solution of diiododimethylfluorescein in 70% v/v aqueous alcohol were used as adsorption indicators[2]. Bromo- and iodo-acids were prepared by methods similar to those as described in a previous paper[1].

Apparatus and procedure

Whatman's No. 4 filter paper purified by chromatographic washing[3] with $2N$ acetic acids, distilled water and $10N$ ammonia was used throughout. The acids was dissolved in dilute aqueous ammonia, and the resulting solution of their ammonium salts was applied to the chromatograms with a micropipette. A convenient one may be made in the laboratory[3]. The developing solvent contained 70% propanol and 30% concentrated ammonia.

A "guide" chromatogram was always run alongside the main chromatogram and the position of the acids was located only on the guide chromatogram by the procedure of HASHMI AND CULLIS[1]. 4 and 5 µg is the detection limit for bromo- and iodo-acids respectively. The acids on the main chromatogram was located by comparison to a guide chromatogram.

The piece of paper containing the ammonium salts of the acid was cut out of the chromatogram and refluxed for about 2 hours in a 250 ml flask with 20 ml of absolute alcohol and 1-2 g of metallic sodium with occasional shaking of the flask[4,5]. The products were allowed to cool and were diluted by cautious addition of water through the condenser, 1 ml at a time being added at first until the vigorous action has ceased. The total volume of the solution should not exceed 50 ml. The solution, while kept cool with tap water, was neutralised with $6N$ halogen-free nitric acid using phenolphthalein as indicator, and a further 5 ml of acid were then added. The halogens were determined

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by direct titration against silver nitrate using eosin and diiododimethylfluorescein as indicators for bromo- and iodo-acids respectively.

"Blank" determinations were made to ensure that the paper and substances present in the paper do not affect the results.

RESULTS

A large number of bromo- and iodo-acids were estimated by this method. The results show that almost all the acid ($\geqslant$ 98%) could be estimated accurately.

TABLE I

QUANTITATIVE ESTIMATION OF SOME BROMO-ACIDS ON PAPER CHROMATOGRAMS

Acid	*Amount added*[a] *(μg)*	*Amount found* *(μg)*	*Recovery* *(%)*
$CH_2Br\cdot COOH$	34.2	33.9	98.8
	47.3	46.4	98.1
	32.9	32.1	97.6
$CH_3\cdot CHBr\cdot COOH$	39.8	39.2	98.4
	43.6	43.1	98.7
	45.4	44.5	98.0
$CH_2Br\cdot CH_2\cdot COOH$	27.7	27.2	98.2
	45.9	45.1	98.3
	46.7	46.1	98.7
$CH_3\cdot CH_2\cdot CHBr\cdot COOH$	41.6	40.8	98.5
	59.2	58.2	98.3
	40.8	40.1	98.3
$(CH_3)_2CBr\cdot COOH$	37.3	36.5	98.0
	42.9	42.1	98.1
	65.3	64.2	98.3
$CH_3\cdot (CH_2)_2\cdot CHBr\cdot COOH$	45.2	44.5	98.3
	22.8	22.2	97.9
	61.3	60.4	98.5
$(CH_3)_2CH\cdot CHBr\cdot COOH$	42.9	42.2	98.4
	37.5	36.8	98.1
	63.7	62.7	98.4

[a] The weights refer to free bromo-acids, although they were added as ammonium salts.

TABLE II

QUANTITATIVE ESTIMATION OF SOME IODO-ACIDS ON PAPER CHROMATOGRAMS

Acid	*Amount added*[a] *(μg)*	*Amount found* *(μg)*	*Recovery* *(%)*
$CH_2I\cdot COOH$	47.6	46.8	98.3
	25.8	25.2	98.0
	38.6	38.3	99.1
$CH_3\cdot CHI\cdot COOH$	32.5	31.9	98.1
	63.6	62.8	98.8
	43.6	43.2	99.1
$CH_2I\cdot CH_2\cdot COOH$	46.7	46.1	98.6
	46.7	45.8	98.1
	54.3	53.2	98.0
$CH_3\cdot CH_2\cdot CHI\cdot COOH$	35.9	35.1	97.9
	37.5	36.9	98.4
	42.8	42.1	98.3
$(CH_3)_2CI\cdot COOH$	66.3	65.5	98.8
	49.2	48.3	98.2
	45.7	45.1	98.5
$(CH_3)_2CH\cdot CHI\cdot COOH$	47.2	46.4	98.3
	36.1	35.6	98.8
	33.9	33.3	98.2

[a] The weights refer to free iodo-acids, although they were added as ammonium salts.

Some results on the analysis of made-up mixtures of bromo- and iodo-acids are given in Table III. The mixture could be separated into different acids on a paper chromatogram by the procedure of HASHMI AND CULLIS[1]. The paper strip containing the acids was cut out of the chromatogram and each acid was estimated separately as described previously.

TABLE III

ESTIMATION OF MIXTURES OF BROMO- AND IODO-ACIDS ON PAPER CHROMATOGRAMS

Components present	*1st component (μg)*		*2nd component (μg)*	
	Amount added	*Amount found*	*Amount added*	*Amount found*
$CH_2I\cdot COOH$, $CH_2Br\cdot COOH$	33.7	33.1	45.9	45.2
$CH_3\cdot CH_2\cdot CHBr\cdot COOH$, $CH_2I\cdot COOH$	51.6	50.8	38.5	37.9
$CH_2I\cdot CH_2\cdot COOH$, $(CH_3)_2CI\cdot COOH$	32.1	31.7	29.8	29.2
$CH_2Br\cdot COOH$, $CH_3\cdot CH_2\cdot CHBr\cdot COOH$	42.5	41.8	36.7	35.8
$CH_3\cdot CHI\cdot COOH$, $CH_2Br\cdot COOH$	36.3	35.8	41.3	40.5

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SUMMARY

A quantitative method is described for the estimation of the ammonium salts of the halogenated organic acids after they have been separated on a paper chromatogram. The recovery of the added acid is better than 98%.

RÉSUMÉ

Une méthode quantitative est décrite pour le dosage des sels d'ammonium des acides organiques halogénés, après séparation par chromatographie sur papier. Par ce procédé, on peut retrouver plus de 98% de la teneur en acide.

ZUSAMMENFASSUNG

Eine quantitative Methode zur Bestimmung der Ammoniumsalze der halogenierten organischen Säuren nach deren Trennung auf einem Papierchromatogramm wird beschrieben. Die zurückgewonnene Menge der zugefügten Säure beträgt mehr als 98%.

REFERENCES

[1] M. H. HASHMI AND C. F. CULLIS, *Anal. Chim. Acta*, 14 (1956) 336.
[2] H. B. FELDMAN AND A. L. POWELL, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 89.
[3] F. A. ISHERWOOD AND C. S. HANES, *Biochem. J.*, 55 (1953) 824.
[4] I. DROGIN AND M. A. ROSANOFF, *J. Am. Chem. Soc.*, 38 (1916) 711.
[5] R. R. UMHOFFER, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 383.

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ELECTRO-CHROMATOGRAPHY IN THE SEPARATION OF IONS.
PART II. SEPARATION OF PRECIOUS METALS

by

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Electro-chromatography since its introduction in 1951 has proved to be an effective analytical tool for the detection, separation and determination of both organic and inorganic ions and for the study of the nature and the stability of the complexes.

MAJUMDAR AND MUKHERJEE[1] have successfully separated some of the sulphide group elements from each other. Many attempts by workers in this field for the separation of elements, common and rare, have been made, though no systematic work on the study of the separability of the precious metals Pt, Pd, Os, Ir, Ru, Rh and Au has yet been made. LEDERER and his collaborators[2,3], however, tried the separation of Cu from Au, Pt and Pd, Hg from Pd and Pt from Pd.

The remarkable properties of the precious metals Pt^{+4}, Ir^{+4}, Os^{+4}, Ru^{+3}, Rh^{+3}, Au^{+3}, Pd^{+2}, for complex formation have been used in an attempt, reported in this paper, to separate them from each other. From solutions of different groups of three or four elements it has been found possible to separate the elements from each other in distinct zones when they are present in microgram quantities.

EXPERIMENTAL

The apparatus and the technique adopted with Whatman filter paper No. 2, cut into strips of 44 cm × 1 cm, were the same as reported in an earlier paper[1] and a potential of about 150 volt for 5 hours was maintained in every experiment.

Decinormal solutions of the following electrolytes were prepared from the chemicals of highest purity: HCl, H_2SO_4, HNO_3, H_3PO_4, CH_3CO_2H, $H_2C_2O_4$, NH_4OH, NaOH, Na_2CO_3, $NaHCO_3$, $(NH_4)_2CO_3$, NH_4Cl, NaCl, KCl, NaBr, KBr, NH_4CNS, $NaNO_2$, KI, KCN, $Na_2S_2O_3$, CH_3CO_2Na, $CH_3CO_2NH_4$, $CS(NH_2)_2$(pH about 5), $CS(NH_2)_2$(in 0.1*N* HCl), $CS(NH_2)_2$(in 0.1*N* NH_4OH), tartaric acid, Na-K-tartrate, citric acid, Na-citrate and complexone III.

Attempts at separation with 1*N* solutions of the salts as electrolytes were not satisfactory as the high concentration of the electrolytes generated much heat during electrolysis and decreased the electro-osmotic flow by the salting effect.

Chloride solutions of Au^{+3}, Pt^{+4}, Pd^{+2}, Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4} of approximately the same strength containing only microgram amounts of the metals were used and about 0.01 ml of the ternary or the quaternary mixture was spotted in the centre of the filter paper. After the experiment the paper strips were dried in air and the zones were located by spraying with suitable developing agents. When potassium cyanide and complexone III were used as electrolytes, the complexes were decomposed by spraying with acid before the ions were identified. The ionic movements recorded in Table I were obtained by measuring the distance from the centre of the original spot to the centre of the spot after electrochromatographic development.

DISCUSSION

Table I shows the effect of electrolyte on ionic movement, and the sequences of separation are shown in Table II. Movements of the ions towards the anode are indicated

TABLE I

THE EFFECT OF ELECTROLYTES ON THE IONIC MOVEMENTS

Electrolytes	*Pd* *cm*	*Pt* *cm*	*Ir* *cm*	*Rh* *cm*	*Au* *cm*	*Ru* *cm*	*Os* *cm*
NH_4Cl	—3.0	8.1	—5.3	4.9 1.0	0.3	0.6	8.4
NaCl	6.2	11.1	—8.5	0.0	2.5	—0.3	7.8 3.5
KCl	8.5	9.8 6.5	—7.2	4.2 0.5	5.1	—	8.2
HCl	5.5	3.7 1.4	—2.8	2.4 0.0	2.6	—	3.5
HNO_3	1.9	2.4	—1.4	2.1	—2.0	—0.3	4.0
H_2SO_4	2.0	2.8	—6.0	2.1 —1.7	3.4	—0.9	8.0
NH_4OH	—13.2	—0.2 —4.2	—1.6	0.2	0.0	—0.4	—0.4
NaOH	1.1	—	—0.4	—0.3	0.2	—1.2	1.5 —1.1
$NaHCO_3$	0.3	11.7	—1.0	9.7	0.1	—1.1	1.4 —0.4
$(NH_4)_2CO_3$	—15.4	—1.2 —8.6	—1.6	—0.1	0.0	—0.6	—0.2
Na_2CO_3	0.6	14.1	—0.4	12.4 0.0	0.2	—2.5	1.0
$NaNO_2$	10.5	9.1	—8.2	—	0.0	—	5.7
KI	0.0	7.9	—7.7	—1.6	—	—	—
NaBr	11.8	15.1 10.2	—8.1	0.0	5.1	—	13.2
KBr	9.7	10.2 8.1	—8.5	—1.2	5.2	—	10.5
$H_2C_2O_4$	5.9	8.0	—3.0	6.0	0.6	—	4.6
CH_3CO_2H	—0.7	2.3	—1.4	—0.2	2.0	—1.0	—0.8
$CH_3CO_2NH_4$	—12.1	8.0	—6.6	0.8	0.0	—	1.3
CH_3CO_2Na	1.2	10.8	—6.8	2.4 0.0	0.4	—	1.3
H_3PO_4	1.7	8.8 5.7	—10.1	4.4 —0.4	2.6	—	4.5
$Na_2S_2O_3$	4.9 0.0	7.9	—4.2	4.0 —0.9	—	0.0	5.4
$CS(NH_2)_2$(in 0.1*N* HCl)	—2.3	—2.6	—2.7	0.6	—	—0.9	4.2
$CS(NH_2)_2$ (pH about 5)	—0.2 —1.7 —4.7	—4.4	—3.9	0.0	0.0	—2.6	5.2
$CS(NH_2)_2$(0.1*N* NH_4OH)	0.1	—0.1	—2.3	0.2	0.0	0.1 —2.1	1.2
NH_4CNS	9.5	7.6	—4.7	—0.3	9.0	—	9.8
KCN	13.6	—	11.5	—	—	—	2.3
Complexone III	5.9	8.7	—	—	0.5	—	8.2
Citric acid	1.0	4.5	—6.3	—0.2 —1.8	3.2	—1.3	—0.3
Na-citrate	7.2	10.5	6.5	6.0	0.8	1.1	6.7
Tartaric acid	0.9	4.7	—9.3	1.4 —0.8	2.5	—1.2	—0.5
Na-K-tartrate	6.5	10.5	0.9	5.2	0.9	—	4.2

by the + sign, movements towards the cathode by the — sign: the ions that move partly towards the anode and partly towards the cathode are given in parentheses. The starting point is marked by a colon.

TABLE II

Electrolytes (0.1N)	*Sequence of separation*
HCl	+ Pd, Rh: Ir—; + Pd, Pt: Ir—; + Pd, Os: Ir—; + Pd, Au: Ir—
H_2SO_4	+ Pt, Rh: Rh, Ir—; + Os, Pd: Ir—; + Os, Au: Ru, Ir—; + Os, Au: (Rh), Ir—
HNO_3	+ Os, (Pd): Ir—; + Pt, Ru: Ir—; + Os, Rh: Ir—
NH_4OH	: Au, Ir, Pd—; :Pt, Ir, Pd—
NaCl	+ Pd: Rh, Ir—; + Pt, Rh, Au: Rh, Ir—; + Os, Rh, Au: Rh, Ir—
NH_4CNS	+ Pd: Rh, Ir—; + Pt: Rh, Ir—; + Os: Rh, Ir—; + Au: Rh, Ir—
$NaNO_2$	+ Pd, Au: Ir—; + Pt, Au: Ir—; + Os, Au: Ir—
$(NH_4)_2CO_3$	+ Pt, Au: Pd—; + Pt: Ir, Pd—
CH_3CO_2Na	+ Pt, Au: Ir—; + Pt, Pd: Ir—
Na_2CO_3	+ Pt, Au: Ir—
$H_2C_2O_4$	+ Pd, Au: Ir—; + Pt, Au: Ir—; + Rh, Au: Ir—; + Os, Au: Ir—
Na-citrate (Neutral)	+ Pt, Ir, Au:; + Pt, Os, Au:; + Pt, Pd, Rh, Au:
Complexone III	+ Pt, Pd, Au:; + Os, Pd, Au:
Tartaric acid	+ Pt: Rh, Ir—; + Os, Au: Ir—
$CS(NH_2)_2$ in 0.1*N* HCl	+ Os: Ru, Ir—
$CS(NH_2)_2$ in 0.1*N* NH_4OH	: Pd, Os, Ir—
NH_4Cl	+ Pt, Rh: Pd, Ir—; + Os, Rh: Pd, Ir—; + Pt, Rh, Au: Ir—; + Os, Rh, Au: Ir—
KCl	+ Pd, Au: Rh, Ir—; + Pt, Au: Rh, Ir—; + Os, Au: Rh, Ir—
KI	+ Pt, Pd: Rh, Ir—
$Na_2S_2O_3$	+ Pt, Pd: Rh, Ir—; + Pt, Os: Rh, Ir—
KBr or NaBr	+ Pt, Au: Rh, Ir—; + Pd, Au: Rh, Ir—; + Os, Au: Rh, Ir—
$CH_3CO_2NH_4$	+ Os, (Au): Ir, Pd—; + Pt, (Au): Ir, Pd—
$CS(NH_2)_2$ (pH about 5)	+ Os, (Au): Ru, Ir—; + Os, (Au): Ru, Pt—; + Os, (Rh): Ru, Ir—; + Os, (Rh): Ru, Pt—
Na-K-tartrate	+ Pt, Os, Pd, Au:; + Pt, Os, Pd, : Ir—

Occasionally, in duplicate and triplicate analysis some variations in the ionic movements are noticed but the sequence remains the same (see Table II). The figures recorded in Table I are the mean values of several observations and the failures to detect the bands are represented by dashes. Under the conditions adopted in this experiment the degree of reproducibility of the results is highly satisfactory as confirmed by repetition. Separation with electrolytes as NaOH, $NaHCO_3$, KCN, H_3PO_4, CH_3CO_2H and citric acid is not satisfactory.

Moistening of the paper strips with the electrolytes sometimes results in the reduction of the metallic ions to the lower valence state or to the formation of precipitates. In some cases formation of more than one band towards the same electrode is observed. This may be explained as due to change in the valency of the metallic ions and/or due to soluble complex and insoluble simple compound formation with the electrolytes. This effect is noticed in the case of Rh in presence of NH_4Cl, KCl, Na_2CO_3, CH_3CO_2Na and citric acid, Pt in KCl, HCl, NH_4OH, $(NH_4)_2CO_3$, H_3PO_4, NaBr, KBr and $CS(NH_2)_2$ (pH about 5), Os in NaCl and Pd in $Na_2S_2O_3$. Appearance of spots towards both the electrodes implies the presence of two ionic species in the complexed solution; one may be anionic (the complex) and the other cationic (the simple ion), *e.g.* Rh in presence of H_2SO_4, H_3PO_4, $Na_2S_2O_3$ and tartaric acid, Os in NaOH and Na_2CO_3 and Ru in thiourea (in 0.1*N* NH_4OH).

Other interesting facts that have emerged are the following. Pd is anionic in KCN, NaCl, KCl and CH_3CO_2Na but cationic in NH_4Cl, CH_3CO_2H and $CH_3CO_2NH_4$. Ir is anionic only in KCN, Na-citrate and Na-K-tartrate (see Table I), but when present in a mixture of platinum metals it becomes cationic in Na-K-tartrate (see Table II). Pt is anionic in Na_2CO_3 and $NaHCO_3$ but cationic in NH_4OH and $(NH_4)_2CO_3$ and Os is anionic only in KCN solution.

Results recorded in Table II show that from different mixtures of three or four precious metals it is possible to separate elements from each other in distinct zones with quite a large number of electrolytes, the latter acting usually as complexing agents effect the separations which are due to different degrees of dissociation of the complexes.

SUMMARY

An electrochromatographic study of the migration rates and sequences of the precious metals, as Pt^{+4}, Os^{+4}, Ir^{+4}, Ru^{+3}, Rh^{+3}, Au^{+3} and Pd^{+2}, on paper strips, reveals that quite a large number of electrolytes effectively separate in distinct zones at least four ions present in microgram amounts in a mixture, when the voltage is maintained at 150 V for 5 hours.

RÉSUMÉ

Une étude électro-chromatographique des vitesses et des séquences de migration des métaux précieux (Pt^{+4}, Os^{+4}, Ir^{+4}, Ru^{+3}, Rh^{+3}, Au^{+3} et Pd^{+2}) sur bandes de papier a montré qu'un grand nombre d'électrolytes permettent de séparer en zones distinctes au moins 4 ions d'un mélange en quantités microchimiques; le voltage doit être maintenu à 150 V pendant 5 heures.

ZUSAMMENFASSUNG

Eine elektrochemische Untersuchung der Wanderungsgeschwindigkeiten und -Reihenfolgen der Edelmetalle wie Pt^{+4}, Os^{+4}, Ir^{+4}, Ru^{+3}, Rh^{+3}, Au^{+3} und Pd^{+2} auf Papierstreifen zeigt, dass eine recht grosse Anzahl von Elektrolyten wenigstens vier Ionen, welche in Mikrogramm-Mengen in einem Gemisch enthalten sind, wirksam in deutliche Zonen scheidet wenn die Spannung während fünf Stunden auf 150 Volt gehalten wird.

REFERENCES

[1] A. K. Majumdar and H. G. Mukherjee, *Anal. Chim. Acta*, 15(1956) 547.

[2] M. Lederer and F. L. Ward, *Australian J. Sci.*, 13 (1951) 114; *Anal. Chim. Acta*, 6 (1952) 355.

[3] M. Lederer, *Introduction to Paper Electrophoresis and Related Methods*, 2nd impression, Elsevier Publishing Co., Amsterdam, 1957.

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INFRARED SPECTRA OF OXINE CHELATES

by

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The infrared spectra of a number of 8-quinolinol chelates have been previously published[1,2], but an investigation of the full range from 2-15 μ for most of these compounds has not been made, principally because they are insufficiently soluble in the usual spectrographic solvents and mulls have considerable portions of the spectrum obscured by hydrocarbon bands.

In this work chelates or salts of 8-quinolinol with 33 metals have been examined in potassium bromide pellets throughout the wavelength range 2-15 μ. It was found, as expected, that the spectra were characterized by extremely close similarity of band positions, with a few exceptions due to hydration and the presence of oxygen-containing cations, and with greater variability above 11 μ than at shorter wavelengths. However, the relative intensities of many of the bands were sufficiently variable from metal to metal to warrant intensity as well as wavelength comparison for purposes of qualitative identification. Since it is rather troublesome to control concentrations in potassium bromide pellets, the intensity of each band was compared to that of the distinctive 9 μ band within the same spectrum rather than to any absolute standard.

Water of hydration in the chelates was readily detected as a very broad band near 3 μ. The intensity ratio to the 9 μ band is 0.30 ± 0.05 for one, and 0.60 ± 0.05 for two, molecules of water per molecule of chelate. Cadmium oxinate dihydrate was the only exception to this rule; the intensity ratio for it was 0.88. Compounds that were not hydrated sometimes showed C-H bands in this region that could possibly be mistaken for hydration except that the intensity ratios of these bands were always smaller than 0.17. The poor resolution from 2-4 μ as well as the partial opacity of the pellets was unfavorable for further structure assignments in this region, since even the C-H frequency could not always be detected.

From 4 to 6 μ there was negligible absorption by all the chelates and it may be concluded that no carbonyl groups are present, although ketone structures for 8-quinolinol chelates have been proposed occasionally in the literature[3].

There were many strong bands in the range 6 to 8 μ, most of them classed as aromatic ring vibrations[4]. Bands at 6.27-6.37, 6.60-6.67, 6.75-6.84 and 7.46-7.57 μ were all strong. A band at 7.11-7.26 and one at 7.20-7.32 μ frequently appeared to overlap so that one of the two was partially or totally obscured in many of the spectra. A band at 6.94-7.03 μ was the only one in this region of characterization value, showing very strong for the alkali metal salts and varying in relative intensity from 0.16 to 0.9 for the other chelates. No systematic rule for these intensity variations as a function of structure was apparent, however.

A medium intensity band at 8.0-8.2 and a weak band at 8.47-8.55 were the only notable features of the 8-9 μ region. The most characteristic feature in all the spectra is the sharp, intense absorption at 8.97-9.07 μ that is used as a reference point for the intensity measurements. Although the position of this band is said to vary with the stability of the chelate[1], our instrument was not sufficiently precise to detect this effect with any confidence.

At 11.08 or 11.09 μ there is a strong absorption by the molybdenum, tungsten and uranium chelates that is lacking or very faint in all the other spectra. This band must result from the MO_2^{+2} combination that is present only in these compounds.

In the 12-13.5 μ region there are usually four rather strong bands at 12.00-12.24, 12.32-12.46, 12-59-12.70 and approximately 13.40 μ but the positions and relative intensities of these bands are subject to considerable variations from compound to compound. (The titanium compound shows only two very broad maxima in the 12-14 μ range.)

From 13.6 to 14.1 μ there are single strong bands shown by the sodium, potassium, silver nitrate, strontium, barium, lanthanum, lead, thorium, vanadium, antimony, bismuth, uranium, palladium, cerium, neodymium and samarium derivatives only.

In addition to the above catalog of maxima a few of the compounds show individually characteristic features, mostly in the 12-15 μ region. The close similarity of the silver

nitrate compound[5] to oxine itself rather than to the other metal derivatives suggests that this substance is an addition compound and not a chelate or salt.

EXPERIMENTAL

The chelates and salts were prepared by standard procedures[6,7], and air dried at room temperature. They were then analyzed either by the well-known bromometric method or by ignition to the metal oxide. The palladium derivative was reduced to the metal for weighing. The results of the analyses corresponded to the following formulas (in which HOx stands for C_9H_7NO): LiOx, NaOx, KOx, $CuOx_2$, $AgNO_3\cdot(HOx)_2$, $MgOx_2\cdot 2H_2O$, $ZnOx_2\cdot 2H_2O$, $SrOx_2\cdot 2H_2O$, $CdOx_2\cdot 2H_2O$, $BaOx_2$, $AlOx_3$, $GaOx_3$, $InOx_3\cdot H_2O$, $LaOx_3$, $TiOOx_2\cdot H_2O$, ZrO_2Ox_3, $PbOx_2$, $ThOx_4\cdot HOx$, $V_2O_3Ox_4$, $SbOx_3$, $BiOx_3\cdot H_2O$, $CrOx_3\cdot H_2O$, MoO_2Ox_2, WO_2Ox_2, $UO_2Ox_2\cdot HOx$, $MnOx_2\cdot 2H_2O$, $FeOx_3$, $CoOx_2\cdot 2H_2O$, $NiOx_2\cdot 2H_2O$, $PdOx_2$, $CeOx_4$, $NdOx_3$ and $Sm(OH)Ox_2\cdot H_2O$. It is probable that the zirconium and samarium derivatives are of indefinite composition[8] but the analyses corresponded very well to the formulas written. Attempts to prepare the red ferrous chelate in the solid state failed because of its very rapid oxidation in air.

The infrared spectra were run on a Baird Associates double-beam spectrophotometer with NaCl optics, using the micro pellet holder manufactured by this firm for the KBr pellets. Band intensities were measured by the well-known base line technique.

ACKNOWLEDGEMENT

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SUMMARY

The infrared spectra of thirty-three oxine chelates were run in the wave-length range from 2-15 μ. By comparison of both wavelength and intensity of the absorption bands, water of crystallization can be determined, the tungsten, uranium and molybdenum and titanium chelates can be conclusively identified and distinctive characterization of most of the other chelates is also possible.

RÉSUMÉ

Les spectres infrarouges de 33 chélates de l'oxine ont été déterminés dans les longueurs d'onde de 2 à 15 μ. Par comparaison de la longueur d'onde et de l'intensité des bandes d'absorption, l'eau de cristallisation peut être déterminée, les chélates du tungstène, de l'uranium, du molybdène et du titane peuvent être ainsi identifiés et la caractérisation de la plupart des autres chélates est généralement possible.

ZUSAMMENFASSUNG

Die Infrarot-Spektren von 33 Oxin-Chelaten wurden in dem Wellenlängenbereich von 2-15 μ aufgenommen. Durch Vergleich von Wellenlänge und Intensität der Absorptionsbanden kann des Kristallisationswasser bestimmt werden, Wolfram-, Uran-, Molybdän- und Titan-Chelate können mit Sicherheit identifiziert werden, und eine Charakterisierung der meisten anderen Chelate ist ebenfalls möglich.

REFERENCES

[1] R. G. CHARLES, H. FREISER, R. FRIEDEL, L. E. HILLIARD AND W. D. JOHNSTON, *Spectrochim. Acta*, 8 (1956) 1.
[2] K. G. STONE, *J. Am. Chem. Soc.*, 76 (1954) 4997.
[3] M. SEGUIN, *Bull. soc. chim. France*, (1946) 566.
[4] L. J. BELLAMY, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, 1954.
[5] F. HEIN AND H. REGLER, *Ber.*, 69B (1936) 1692.
[6] F. J. WELCHER, *Organic Analytical Reagents*, D. Van Nostrand, New York, 1947.
[7] R. G. W. HOLLINGSHEAD, *Oxine and Its Derivatives*, Butterworths Scientific Publications, London, 1954.
[8] J. P. PHILLIPS, *Chem. Revs.*, 56 (1956) 271.

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ÜBER DIE VERTEILUNG VON METALL-8-OXYCHINOLIN-VERBINDUNGEN ZWISCHEN WASSER UND ORGANISCHEN LÖSUNGSMITTELN

3. MITT. PHOTOMETRISCHE BESTIMMUNG DES MAGNESIUMS NACH EXTRAKTION SEINES OXINATES MIT CHLOROFORM BEI GEGENWART VON AMINEN*

von

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Magnesium bildet mit 8-Oxychinolin (Oxin) eine in Wasser schwer lösliche Verbindung $MgOx_2 \cdot 2H_2O$, die mit Vorteil zur gravimetrischen[1,2] oder — über die bromatometrische Titration des Oxins[3] — zur volumetrischen Bestimmung des Magnesiums herangezogen wird. Da es nur wenige brauchbare Methoden zur photometrischen Bestimmung kleiner Magnesiummengen gibt, hat man auch wiederholt versucht, das Magnesiumoxinat dafür einzusetzen, indem man es durch Fällung und Filtration isolierte und in einer zweiten Reaktion das gebundene Oxin zu einer gefärbten Lösung umsetzte, z.B. durch Auflösen in Säure und direkte Bestimmung des gelben Oxiniumions, durch Kupplung des Oxins mit diazotierten Aminen zu einem Azofarbstoff oder durch Umsetzung zu dem intensiv gefärbten und auch in organischen Lösungen löslichen Eisenoxinat[4]. Alle diese Methoden haben aber den Nachteil der gravimetrischen Bestimmung, dass sie an die relativ geringe Fällungsempfindlichkeit und relativ grosse Löslichkeit des Magnesiumoxinates (*ca.* 0.3 mg in 100 ml)[5] gebunden sind und sich deshalb wenig für die Bestimmung kleiner Mengen Magnesium eignen.

Das Magnesiumoxinat direkt mit einem organischen Lösungsmittel aus der wässrigen Phase zu extrahieren und in der organischen Phase photometrisch zu bestimmen, scheiterte bisher daran, dass das $MgOx_2 \cdot 2H_2O$ in indifferenten, mit Wasser nicht mischbaren Lösungsmitteln ebenfalls sehr schwer löslich und infolgedessen auch nicht extrahierbar ist. Diese Eigenschaft teilt es mit den Oxinaten anderer zweiwertiger Elemente, wie z.B. Zn und Cd, die zwar zum Teil extrahiert werden können, dabei aber instabile Extrakte geben, die sich nach ganz kurzer Zeit trüben. Alle sich so verhaltenden Elemente haben gemeinsam, dass sie in Komplexverbindungen die Koordinationszahl 6 bevorzugen und ihre Oxinate sehr stabile Dihydrate bilden. Hiernach, sowie auf Grund der röntgenographischen Untersuchungen an dem Zinkoxinat $ZnOx_2 \cdot 2H_2O$[6], kann kein Zweifel bestehen, dass die beiden Wassermoleküle zur Komplexschale gehören. Andererseits ist sicher dieser Wassergehalt der Verbindung für die geringe Löslichkeit der Oxinatdihydrate in organischen Lösungsmitteln verantwortlich. Die durch Erhitzen auf 180° hergestellten wasserfreien Me(II)-Oxinate sind nämlich, wie wir fanden, gut in wasserfreiem Chloroform und anderen organischen Lösungsmitteln löslich. Bei geringem Wassergehalt entsteht jedoch — je nach Wassergehalt und Art des Metalles schneller oder langsamer — eine gelbliche Trübung und das Hydrat des Metalloxinates fällt aus der organischen Lösung aus.

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* 2. Mitt. *Anal. Chim. Acta,* 16 (1957) 334.

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Auf Grund dieser Beobachtungen lag der Gedanke nahe, das zur Komplexschale gehörende Wasser durch polare organische Moleküle zu ersetzen und die Metalloxinate dadurch in organischen Lösungsmitteln löslich zu machen. Unsere Überlegungen wurden gestützt durch die Ergebnisse von LUKE UND CAMPBELL[7], die eine grosse Anzahl organischer Lösungsmittel auf ihre Extrahierfähigkeit für Magnesiumoxinat untersuchten und fanden, dass dieses — wenn auch nicht sehr gut reproduzierbar und nur bei Anwesenheit eines extrem grossen, mehr als 2000-fachen Überschusses an freiem Oxin — mit Acetophenon oder Chloroform-Glykolmonobutyläther-Mischungen zu extrahieren ist.

Zur Prüfung unserer Arbeitshypothese führten wir eine Anzahl von Vorversuchen mit verschiedenen zweiwertigen Metallen (Mg, Zn, Cd, Hg, Be, Cu, Ca, Sr, Ba, Pb) und verschiedenen polaren organischen Reagentien durch[8]: Je 50 ml $10^{-4} M$ Me(II)-Salzlösungen, die gleichzeitig $0.1 N$ an KNa-Tartrat und $0.1 N$ an einer geeigneten Puffermischung (pH-Bereich etwa 6-13) waren, wurden mit einigen Prozenten des auf seine Wirksamkeit zu prüfenden Reagenses versetzt und anschliessend 1-2 Minuten mit je 50 ml Oxin-Chloroformlösungen variabler Konzentration ausgeschüttelt. Das Spektrum der Chloroformlösungen wurde mit einem Spektralphotometer (Sp. 500 der Firma Unicam) vermessen und mit dem einer unter gleichen Bedingungen, jedoch ohne Zusatz des zu prüfenden Reagenses hergestellten Vergleichslösung verglichen. Die Ergebnisse dieser Untersuchungen, über die später ausführlicher berichtet werden soll, lassen sich kurz folgendermassen zusammenfassen:

Von ganz wenigen Ausnahmen abgesehen, haben polare organische Reagentien gleicher Konstitution auch etwa die gleiche Wirkung auf die Extraktion aller Me(II)-Oxinate:

Einfache Äther und *Ketone* (Ausnahme bei Hg(II)) haben keinen merklichen Einfluss.

Bei Gegenwart *einfacher aliphatischer Alkohole* ist die Extraktion begünstigt, aber nicht vollständig. Für analytische Zwecke erscheint deshalb die Extraktion bei Gegenwart von Alkoholen wenig geeignet. Dagegen eignen sich kleine, nachträgliche Alkoholzusätze zur chloroformischen Oxinatlösung ausgezeichnet zur Stabilisierung dieser Lösungen (Verhinderung von Trübungen). Diese Versuche zeigen, dass in dem von LUKE UND CAMPBELL verwendeten Chloroform-Glykolmonobutyläther-Gemisch die freie alkoholische OH-Gruppe des Glykols wirksam ist.

Die beste Wirkung auf die Extraktion der Me(II)-Oxinate mit Chloroform wurde bei Zusatz von *einfachen primären* oder *sekundären aliphatischen Aminen* erhalten. Folgendes Beispiel zeigt die Überlegenheit der Amine: Bei Gegenwart von 4% Monobutylglykol wurden aus einer $10^{-4} M$ Mg-Salzlösung bei etwa pH 11 mit einer 1%-igen Oxin-Chloroformlösung nur etwa 30% des Mg extrahiert. Dagegen war unter sonst gleichen Bedingungen bei Zusatz von 2% *n*-Butylamin die Extraktion schon mit einer nur 0.1%igen (*ca.* $0.007 M$) Oxin-Lösung vollständig. Im folgenden wurde ausschliesslich das *primäre* n-*Butylamin* verwendet, doch sind mit nur kleinen Modifikationen in den Versuchsbedingungen auch das sekundäre *n*-Butylamin und die nahen Homologen der beiden Stoffe geeignet.

Im Falle des Magnesiumoxinates wurde gefunden, dass bei Gegenwart von Butylamin eine Verbindung extrahiert wird, die auf ein Mg-Atom 3 Moleküle 8-Oxychinolin und 1 Molekül Amin enthält. Möglicherweise handelt es sich hierbei um das Butylammoniumsalz einer Tris-(8-oxychinolato)-Magnesiumsäure $[R\cdot NH_3]$ $[MgOx_3]$ und nicht um ein Diamin des Magnesiumoxinates, wie man es nach unserer Arbeitshypothese erwarten könnte.

UNTERSUCHUNGEN AN REINEN MAGNESIUMOXINATLÖSUNGEN IN CHLOROFORM BEI GEGENWART VON *n*-BUTYLAMIN

Alle weiteren Untersuchungen wurden im wesentlichen folgendermassen durchgeführt: 5 ml einer neutralen $10^{-3}M$ $MgSO_4$-Lösung wurden in einem 150 ml fassenden Scheidetrichter mit je 5 ml $1N$ KNa-Tartrat- und $1N$ NH_3-Lösung und 1 ml *n*-Butylamin gemischt und mit Wasser auf 50 ml verdünnt (pH 11.2-11.3). Dann wurde eine Minute mit 50 ml einer $7\cdot 10^{-3}M$ Oxin-Chloroformlösung geschüttelt. Nach Trennung der Phasen wurde die Chloroformschicht abgelassen und durch Schütteln mit einer Spatelspitze wasserfreiem Na_2SO_4 getrocknet. Diese Bedingungen werden im folgenden kurz als *Standardbedingungen* bezeichnet.

Das Absorptionsspektrum einer unter Standardbedingungen hergestellten $10^{-4}M$ Magnesiumoxinat-Lösung in Chloroform bei Gegenwart von *n*-Butylamin wurde — wie oben angegeben — in 1 cm Quarzküvetten gegen eine entsprechend hergestellte Vergleichslösung ohne Mg vermessen und in Abb. 1, Kurve I dargestellt. Bei 380 mμ liegt ein Absorptionsmaximum mit einem molaren dekadischen Extinktionskoeffizienten von $\varkappa_{380} = 5600$. Bei dieser Wellenlänge absorbiert auch das in *ca.* 70-facher Konzentration angewandte freie Oxin bereits merklich (Abb. 1, Kurve II), so dass das Messen gegen eine Vergleichslösung unerlässlich ist.

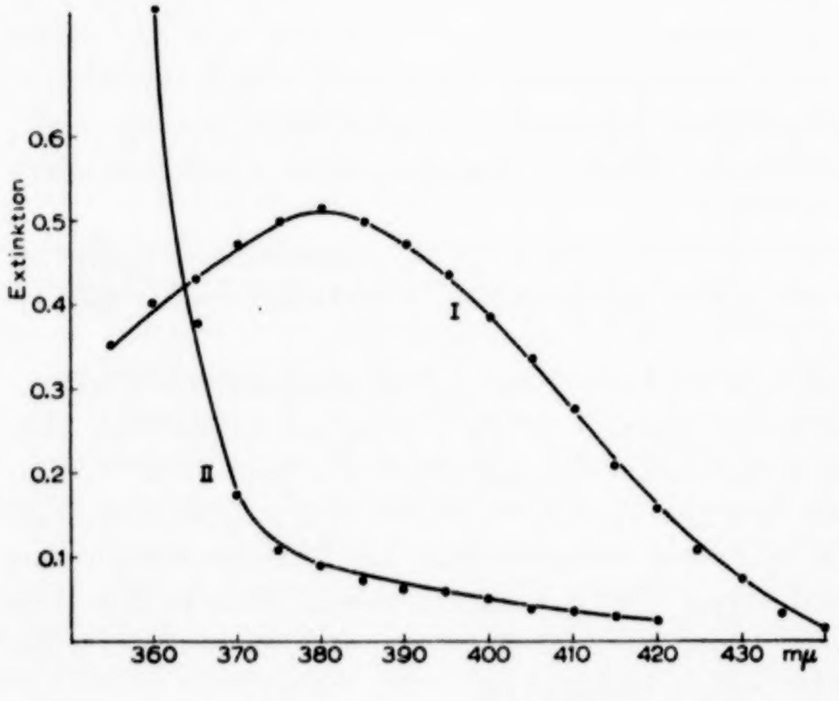

Abb. 1. Kurve I. Spektrum einer $0.94\cdot 10^{-4}M$ Magnesiumoxinat-Lösung in Chloroform bei Gegenwart von *n*-Butylamin.
Kurve II. Spektrum einer $7\cdot 10^{-3}M$ Oxinlösung in Chloroform bei Gegenwart von *n*-Butylamin.

Die späteren Extinktionsmessungen für Reihenversuche führten wir mit dem Filterphotometer „Elko II" der Firma Zeiss in Glasküvetten unter Verwendung des Filters S38E durch. Der „praktische" mol.dek. Extinktionskoeffizient beträgt unter diesen Bedingungen $\varkappa_{S38E} = 5620$ (±80).

Die Spektren des Mg-Oxinates bei Gegenwart verschiedener Amine oder Alkohole unterscheiden sich nicht wesentlich voneinander, d.h., das Absorptionsmaximum liegt immer in der Nähe von 380 mμ.

Des Vergleiches halber versuchten wir auch, eine reine Magnesiumoxinatlösung in Chloroform duch Ausschütteln herzustellen. In kleinen Konzentrationen ist das Mg-Oxinat bei Abwesenheit von Aminen oder Alkoholen nicht nachweisbar zu extrahieren. Erst bei Einsatz von 3 mg Mg in 50 ml der wässrigen Phase wurden nach ganz kurzfristigem Schütteln etwa 0.1-0.3% des Mg im Chloroform gefunden. Bei längerer Schüttelzeit ging die extrahierte Mg-Menge wieder zurück. Offensichtlich entsteht das wasserfreie $MgOx_2$ als Zwischenstufe und wird vorübergehend teilweise extrahiert. Die so hergestellte Chloroformlösung trübte sich jedoch — auch nach sofortiger Trocknung mit Na_2SO_4 — sehr rasch, so dass eine sichere Vermessung des Spektrums nicht möglich war. Es konnte lediglich festgestellt werden, dass die maximale Absorption dieser Lösung sicher nicht bei 380, sondern bei etwa 360 mμ lag.

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Zeitabhängigkeit der Extinktion

Um die Beständigkeit der Magnesiumoxinat-Lösungen in Chloroform bei Anwesenheit von Butylamin zu prüfen, wurden unter den Standardbedingungen unabhängig voneinander zwei $10^{-4}M$-Lösungen hergestellt und mit dem Filterphotometer ,,Elko II", Filter S38E in 2 cm-Küvetten die Änderungen der Extinktion mit der Zeit verfolgt. Wie Tab. I, Spalte I und II zeigen, tritt innerhalb der ersten zwei Stunden nach dem Extrahieren keine wesentliche Änderung der Extinktion auf. Das gilt jedoch nur für Lösungen, die durch Extraktion im pH-Bereich 10.5-11.5 der wässrigen Phase hergestellt wurden. Beim Extrahieren oberhalb pH 11.5 kann es vorkommen, dass die organische Phase sich nach dem Schütteln trübt oder getrübt ist. Zwar verschwindet diese Trübung beim Trocknen mit wasserfreiem Na_2SO_4 schnell, aber es macht sich bereits bei mehr als 30 Minuten nach dem Schütteln ein Abfall der Extinktion bemerkbar. Tab. I enthält unter Nr. III ein Beispiel, bei dem das Mg-Oxinat bei pH 11.8 extrahiert und nur mit Na_2SO_4 getrocknet worden war. Aber auch oberhalb pH 11.5 lassen sich die Chloroformlösungen des Mg-Oxinates über längere Zeit stabilisieren, wenn man ihnen gleich nach der Abtrennung noch etwas Amin oder 4% Methanol zusetzt. Bei Extraktionen oberhalb pH 13 treten Trübungen in der Chloroformphase auf, die durch Trocknen mit Na_2SO_4 nicht mehr zu beseitigen sind, wohl aber durch Zusatz von Methanol (Tab. I, Nr. IV).

TABELLE I

ABHÄNGIGKEIT DER EXTINKTION EINER $10^{-4}M$ MAGNESIUMOXINATLÖSUNG IN CHLOROFORM VON DER STANDZEIT NACH DEM SCHÜTTELN

Standzeit	*Extinktion, gemessen mit Filter S38E (2 cm-Küvetten)*			*(1 cm-Küvette)*
	I	*II*	*III*	*IV*
5 min	1.09	1.09	1.12	0.550
6 ,,	1.09	1.09	1.12	—
10 ,,	1.09	1.09	1.11	0.551
15 ,,	1.09	1.10	1.11	0.550
30 ,,	1.10	1.10	1.12	0.549
1 h	1.11	1.09	1.03	0.550
2 h	1.10	1.08	1.03	0.550
4 h				0.550
15 h				0.547

pH-Wert der wässrigen Phase nach dem Schütteln:
I undII: 11.2-11.3; III : 11.8; IV : 13.1;
Chloroformlösung I-III mit Na_2SO_4 getrocknet, Lösung IV mit 4% Methanol stabilisiert.

Abhängigkeit der Extinktion vom Oxin- und Amingehalt

Das Magnesiumoxinat wurde extrahiert unter Variation der Oxinkonzentration der Chloroformlösung bei konstanter Aminkonzentration (Tab. IIa) und unter Variation des Aminzusatzes zur wässrigen Phase bei konstanter Oxinkonzentration (Tab. IIb). Im übrigen gelten die Standardbedingungen. Tab. II zeigt, dass die Konzentrationen 2% an Butylamin und $7 \cdot 10^{-3}M$ (= *ca.* 0.1 %) an Oxin die optimalen Bedingungen darstellen. Eine weitere Erhöhung der Oxin- oder Aminkonzentrationen bringt keine wesentliche Änderung der Extinktion mehr. Eine weitere Erhöhung der Oxinkonzen-

TABELLE II

ABHÄNGIGKEIT DER EXTINKTION EINER $10^{-4}M$ MAGNESIUMOXINATLÖSUNG IN CHLOROFORM VON DER KONZENTRATION AN OXIN UND *n*-BUTYLAMIN

a) Konst. Butylaminkonz. (2%) der wässr. Ausgangsphase		*b) Konst. Oxinkonz. $7 \cdot 10^{-3}M$ der $CHCl_3$-Lösung vor dem Schütteln*	
Oxinkonz. der $CHCl_3$-Phase M	*Extinktion (Filter S38E, 2 cm-Küvetten)*	*% Butylamin der wässr. Phase*	*Extinktion (Filter S38E, 2 cm-Küvetten)*
0.001	0.040	0.2	0.160
0.002	0.470		
0.003	0.750	0.4	0.340
0.005	0.990	1.0	0.890
0.007	*1.12*	*2.0*	*1.12*
0.021	1.11	4.0	1.16
0.07	1.13	6.0	1.14

tration ist ausserdem unzweckmässig, weil dadurch erstens der Blindwert der Lösung unnötig erhöht und zweitens die Abtrennung des Mg von anderen Elementen (siehe weiter unten) unscharf würde, z.B. geht bei Gegenwart von 2% Amin und Oxinkonzentrationen über 0.02 m das Ca bereits merklich mit in die Chloroformphase. Auch bei Erhöhung des Aminzusatzes können Störungen durch Ca (und Be) auftreten.— Andererseits kann man auch bei geringerer Oxinkonzentration als $0.007M$ die maximale Extinktion erhalten, wenn der Aminzusatz ausreichend erhöht wird und umgekehrt. Jedoch erfordert eine geringe Herabsetzung der Oxinkonzentration eine erhebliche Steigerung des Aminzusatzes und umgekehrt, so dass derartige Variationen der Bedingungen tatsächlich keinen Vorteil bringen. (Betr. Abhängigkeit der Extinktion von der Mg-Konzentration, vgl. unten unter ,,Eichkurve''.)

Die Verteilung des Magnesiumoxinates in Abhängigkeit vom pH-Wert der wässrigen Phase

Die Verteilungskurve des Magnesiumoxinates wurde unter den Standardbedingungen aufgenommen, wobei lediglich der pH-Wert der wässrigen Phase variiert wurde. Zur Einstellung des pH-Wertes bis pH 11.3 wurde der wässrigen Phase HCl zugesetzt, die Gesamtkonzentration an $NH_3 + NH_4^+$ war also immer $0.1N$. Oberhalb pH 11.3 wurde NH_3 nach und nach durch NaOH ersetzt, wobei bei sehr hohen pH-Werten die Konzentration an NaOH natürlich über $0.1N$ hinaus erhöht werden musste.

Der pH-Wert der wässrigen Phase wurde nach dem Schütteln und Ablassen der Chloroformphase mit dem Universal-pH-Messgerät GM 4491 der Firma Philips gemessen unter Verwendung einer hochalkalibeständigen Glaselektrode der Firma Schott, die ohne Korrektur bis pH 12.5 verwendet werden konnte, und einer $1N$ Kalomelelektrode als Bezugselektrode. Geschüttelt wurde in jedem Falle eine Minute. Die Extinktion der organischen Phase wurde mit dem Gerät ,,Elko II'', Filter S38E, in 2 cm-Glasküvetten gemessen. Die Chloroformphase wurde beim Extrahieren oberhalb pH 13 durch Zusatz von 2 ml (4%) Methanol stabilisiert. Die gemessenen Extinktionen wurden mittels der unten beschriebenen Eichkurve in ,,% extrahiert'' umgerechnet und in Abb. 2 in Abhängigkeit vom pH-Wert graphisch dargestellt.

Unter den angeführten Bedingungen beginnt die Extraktion des Magnesiumoxinates bei pH 9.7, ist zwischen pH 10.5 und pH 13.6 vollständig und fällt bei noch höheren pH-Werten wieder stark ab. Die Vollständigkeit der Extraktion wurde geprüft, indem

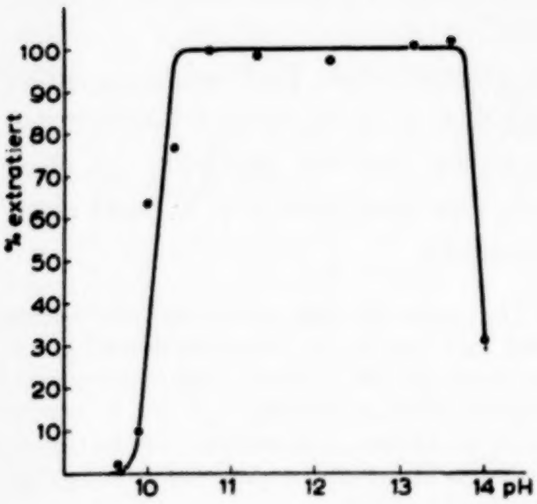

Abb. 2. Abhängigkeit der Verteilung des Magnesiumoxinates vom pH-Wert der wässrigen Phase unter Standardbedingungen.

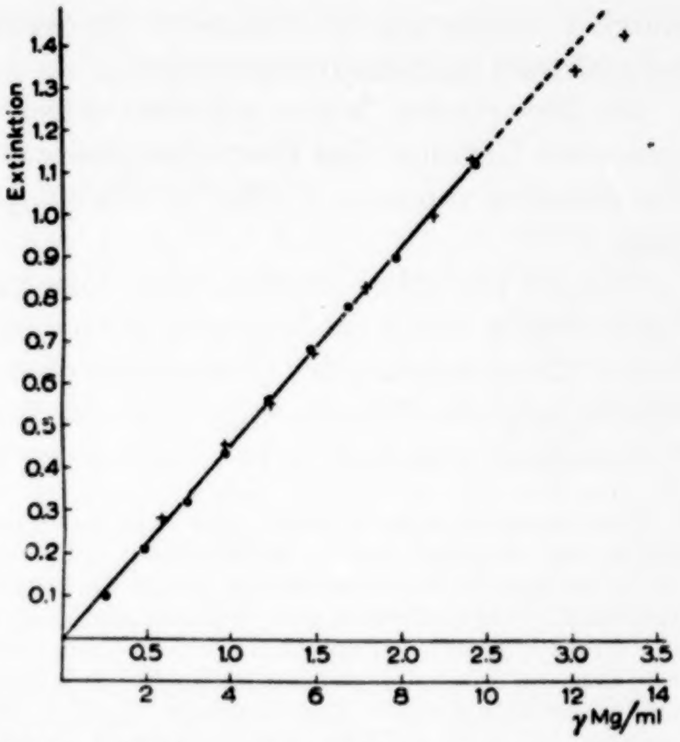

Abb. 3. Eichkurve für die Bestimmung von Magnesium als Oxinat.
- • oberer Abzissenmasstab: Mg-Konz. 0—2.5 γ Mg/ml Chloroform, Extinktionsmessung mit 2 cm-Küvetten.
- + unterer Abzissenmasstab: Mg-Konz. 0—10 γ Mg/ml Chloroform, Extinktionsmessung mit 0.5 cm-Küvetten

die wässrige Phase nach dem ersten Schütteln und sauberer Abtrennung der Chloroformphase nochmals mit 1 ml Butylamin versetzt und ein zweites Mal mit 50 ml 0.1%iger Oxin-Chloroformlösung geschüttelt wurde. Die Extinktion dieser zweiten Lösung lag im pH-Bereich 10.7-13.6 unter 0.01, d.h. — gleiche prozentuale Verteilung in beiden Fällen vorausgesetzt —, dass nach der ersten Extraktion weniger als 1% des Mg in der wässrigen Phase zurückgeblieben ist. Am günstigsten ist die Verteilung bei pH 11.0 ±0.5, oberhalb pH 12 sind die Schwankungen der Messergebnisse grösser, falls — wie in diesem Falle — die Chloroformlösung nicht durch Methanolzusatz stabilisiert wurde. Im Mittel wurden auf Grund der Auswertung mit der Eichkurve zwischen pH 10.5 und 11.5 99.1 (± 0.9)% und zwischen pH 12 und 13.6 100.4 (± 2.3)% Mg in der organischen Phase gefunden.

Aufnahme einer Eichkurve (Abhängigkeit der Extinktion von der Magnesiumkonzentration der wässrigen Phase)

Unter den Standardbedingungen wurde eine Eichkurve aufgenommen, indem die Magnesiumkonzentration der wässrigen Phase zwischen 10^{-5} und 10^{-4} variiert wurde (Abb. 3, Kreise, oberer Abzissenmasstab). Die Extinktionsmessungen beziehen sich auf das Gerät „Elko II", Filter S38E, 2 cm-Küvetten. Um die Magnesiumextraktion möglichst vollständig zu machen, wurde die wässrige Phase (50 ml) nicht einmal mit 50 ml, sondern zweimal mit je genau 25 ml der Chloroformlösung 30 Sekunden geschüttelt. Dabei wurde aber das Mg bereits beim ersten Schütteln praktisch vollständig vom Chloroform aufgenommen, die zweite Fraktion blieb völlig farblos. Man kann also durch Verringerung des Volumens der organischen Phase noch eine Anreicherung bei sehr kleinen Mg-Gehalten erreichen.

Die Messpunkte liegen auf einer durch den Nullpunkt des Koordinatensystems gehenden Geraden. Das Beer'sche Gesetz ist also erfüllt. Die Reproduzierbarkeit der Bestimmung von 0.4-2.5 γ Mg/ml beträgt ± 0.7% (Bestimmung aus reinen Mg-Lösungen).

Wie wir besonders prüften, kann man unter den angegebenen Bedingungen unter Verwendung von 5 cm-Küvetten noch 0.05 γ Mg/ml auf ± 10% genau bestimmen. Unter Herabsetzung des Chloroformvolumens auf 25 ml hat die Methode — ohne Einführung von Mikrogeräten — bei der Bestimmung von insgesamt 1 γ Mg mit einer Genauigkeit von etwa ± 10% ihre untere Grenze erreicht.

Eine Variante besteht darin, dass man mit 2 mal 20 ml Chloroformlösung schüttelt, die beiden Portionen vereinigt, mit 2 ml Methanol (4%) versetzt und mit der Oxin-Chloroformlösung auf 50 ml auffüllt. Diese Arbeitsweise hat für die praktische Bestimmung den Vorteil, dass Chloroformreste von Vorextraktionen (s.u.) nicht so peinlichst genau entfernt werden müssen, dass das Volumen der zum Schütteln verwandten Oxin-Chloroformlösung nicht so genau abgemessen werden muss und dass das Trocknen mit festem Na_2SO_4 sich erübrigt. In beiden Fällen muss natürlich die Extinktion gegen eine entsprechend bereitete Vergleichslösung gemessen werden.

Es wurde auch versucht, die obere Konzentrationsgrenze des Mg festzulegen, bei der eine einwandfreie Bestimmung noch möglich ist. Zu diesem Zweck schüttelten wir wässrige Magnesiumlösungen steigender Konzentration (10^{-4}—$7 \cdot 10^{-4}$) unter den Standardbedingungen einmal mit je 50 ml Oxin-Chloroformlösung aus. Die Extinktionen wurden mit 0.5 cm-Küvetten gemessen und sind zum Vergleich in Abb. 3 (Kreuze!) mit entsprechend vierfach verkleinertem Abzissenmasstab eingetragen. Alle Messpunkte bis 10 γ Mg/ml liegen auf einer Geraden, die sich mit der Eichkurve deckt. Die Reproduzierbarkeit von 2-10 γ Mg/ml beträgt ± 0.8%. Das bedeutet: unter den Standardbedingungen kann man 0.05-10 γ Mg/ml reproduzierbar extrahieren. Das Beer'sche Gesetz ist in dem ganzen Bereich erfüllt. Der Bereich umfasst mehr als zwei Zehnerpotenzen der Konzentration und dürfte normalen analytischen Ansprüchen genügen. Ausserdem zeigt der Vergleich dieser Messreihe mit der Eichkurve (Kreise in Abb. 3), dass man zu identischen Ergebnissen kommt, wenn man 50 ml der wässrigen Phase einmal eine Minute mit 50 ml oder zweimal je 30 Sekunden mit 25 ml der Oxin-Chloroformlösung extrahiert.

DER EINFLUSS ANDERER ELEMENTE UND VERBINDUNGEN AUF DIE EXTRAKTION DES MAGNESIUMOXINATES

Der Einfluss einiger Anionen und Komplexbildner

Im Hinblick auf eine mögliche Tarnung anderer Kationen bei der Extraktion des Magnesiumoxinates wurde der Einfluss einiger Anionen und Komplexbildner bei verschiedenen pH-Werten des wässrigen Phase geprüft, indem die $10^{-4}M$ Mg-Lösung gleichzeitig (im allgemeinen) $0.1 N$ an dem betreffenden Zusatz gemacht und im übrigen die Bedingungen wie bei der pH-Verteilungskurve eingehalten wurden. Tab. III gibt einen Ausschnitt dieser Versuche, wobei die wiedergefundene Menge Mg in Prozenten der eingesetzten Menge ausgedrückt wurde. Daraus folgt:

1) Komplexon III verhindert die Mg-Extraktion im gesamten pH-Bereich.
2) Unvollständige Extraktion resultiert bei Gegenwart von Fluorid und Sulfosalicylsäure.

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TABELLE III

EINFLUSS VON ANIONEN UND KOMPLEXBILDNERN AUF DIE EXTRAKTION DES MAGNESIUMOXINATES BEI VERSCHIEDENEN pH-WERTEN

	Mittlere Extraktion des Mg in % des eingesetzten ($10^{-4}M$)		
	pH: 10.5—11.0	*11.0—11.5*	*12—13*
NH_4F	83—71	71	59—45
Na-Acetat	>56	100	68
Na-Oxalat	100	100	72
Sulfosalizylsäure	∼ 0	15	19—3
KCN	70—100	100	70—50
Komplexon (0.5*N*)	0	0	0
Na_2SO_4 (0.3*M*)	n.b.	100	n.b.
Na_3PO_4 (0.1*M*)	75—100	100	n.b.
Na-Citrat	n.b.	100	n.b.

3) Im analytisch wichtigen pH-Bereich 11.0-11.5 stören nicht Acetat, Oxalat, Citrat, KCN sowie grössere Mengen Sulfat, Chlorid, Phosphat oder Nitrat. Nur im natronalkalischen Gebiet (oberhalb pH 12) wird die Extraktion bei Anwesenheit von Acetat, Oxalat und KCN unvollständig. — Wichtig ist das Verhalten des KCN, weil sich damit die Möglichkeit ergibt, eine grosse Anzahl anderer Kationen im pH-Bereich 11.0-11.5 mit CN^--Ionen zu tarnen.

Das Verhalten anderer Elemente unter den Bedingungen der Magnesiumoxinat-Extraktion

Um einen Überblick zu bekommen, welche Elemente unter den Bedingungen der Magnesiumextraktion ebenfalls in die organische Phase übergehen und wie diese Störungen zu beseitigen sind, wurde das Verhalten aller wichtigen Elemente systematisch untersucht. Dazu wurden im allgemeinen 0.5 g des zu prüfenden Salzes (im allgemeinen Chloride, Nitrate oder Sulfate) gelöst und mit Tartrat und NH_3 versetzt, so dass nach Auffüllen auf 50 ml die Konzentration daran je 0.1*N* war. Dann wurde 1 ml Butylamin zugefügt, der pH-Wert mit Merck'schem Spezialindikatorpapier kontrolliert und erforderlichenfalls mit einigen Tropfen verd. NaOH oder HCl auf 11.0-11.5 korrigiert. Anschliessend wurde eine Minute mit 50 ml Oxin-Chloroformlösung geschüttelt und die Färbung der organischen Phase beobachtet.

Blieb die Chloroformphase farblos, wurde also augenscheinlich nichts extrahiert, so wurden der Lösung 5 ml einer 0.001*M* Mg-Lösung zugesetzt und nochmals eine Minute geschüttelt, um einen eventuellen (auch negativen) Einfluss quantitativ zu erfassen (vgl. Tab. IV).

War jedoch die Chloroformphase gefärbt, liess sich also das zugesetzte Element unter den Bedingungen der Mg-Bestimmung ebenfalls mehr oder weniger stark ausschütteln, so wurde der Versuch wiederholt mit der Abwandlung, dass vor der Extraktion zur Tarnung *ca.* 0.5 g festes KCN oder entsprechend ein anderes geeignet erscheinendes Reagens zugesetzt wurde. Führte das zu keinem Erfolg, so wurde — ohne KCN-Zusatz — versucht, das störende Element durch eine „*Vorextraktion*", dass heisst, bei Abwesenheit von Amin, zu entfernen, wobei unter unseren Bedingungen das Mg quantitativ in der wässrigen Phase bleibt (vgl. S. 236). Ferner wurde geprüft, ob die Vorextraktion bei niedrigeren pH-Werten besser und schneller zum Erfolg führte.

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TABELLE IV

BESTIMMUNG VON 120 γ MAGNESIUM BEI GEGENWART ANDERER ELEMENTE

Element	*Menge mg*	*Tarnung oder Abtrennung*	*Mg gefunden* γ	*% Fehler*
K	260	—	120	±0
Na	390	—	120	±0
Li	80	—	120	±0
Cu	125	KCN	120	±0
Ag	320	KCN	114	−5.0
Ca	100	—	120	±0
Sr	180	—	118	−1.7
Ba	230	—	122	+1.7
Hg^{+2}	270	KCN	125	+4.2
B	35	—	121	+0.8
Seltene Erden	10(Oxyde)	Vorextraktion	122	+1.7
Ti	240	H_2O_2	119	−0.8
Zr	5	Vorextraktion	117	−2.5
As	15	—	122	+1.7
Sb	50	—	121	+0.8
Bi	5	Vorextraktion	118	−1.7
V	175	H_2O_2	116	−3.3
Se^{+6}	25	—	120	±0
Te^{+6}	25	—	118	−1.7
Cr^{+6}	160	—	120	±0
Mo^{+6}	25	—	118	−1.7
W^{+6}	300	—	125	+4.2
U^{+6}	100	H_2O_2	123	+2.5
Ni	100	KCN	115	−4.2

mittlerer Fehler: ±1.7%

Zusammenfassend folgt aus unseren Versuchen:

1. *Alkali-* oder *Erdalkalimetallionen* sowie *Cr(III), Cr(VI), Mo, W, As, Sb, B, Se, Te, Re* und die *Platinmetalle* (ausser *Pd* in grossen Mengen) stören in keinem Falle. *Ca* und *Be* werden nur dann teilweise mitextrahiert, wenn die Oxin- oder Aminkonzentration mehr als dreifach höher ist, als für die Standardbedingungen angegeben. *Sn(IV)* wird zwar nicht extrahiert, verhindert aber die vollständige Mg-Extraktion, wenn es zu mehr als 5 mg vorhanden ist. Grössere Mengen müssen deshalb durch Vorextraktion als Sn(II)-Oxinat oder auf anderem Wege abgetrennt werden.

2. *Ti, V* und *U* können in grosser Menge durch Zugabe von H_2O_2 (1-3 ml 30%iges Perhydrol) getarnt werden.

3. Durch Zugabe von KCN lassen sich grosse Mengen *Cu, Ag, Au, Ni, Pd* und *Hg(II)* tarnen. KCN wird dabei in fester Form in solcher Menge (0.5-1 g) zugesetzt, dass eine klare, wässrige Lösung entsteht. In kleineren Mengen bis zu 10 mg können getarnt werden: *Zn, Cd* und *Fe(II)*. *Fe(III)* kann nach vorheriger Reduktion mit SO_2, *Hg(I)* entsprechend nach Oxydation zu Hg(II) mit KCN getarnt werden.

4. Bis zu 15 mg *Al* können durch Zusatz von Triäthanolamin (je 1 ml für 2.5 mg Al) in der wässrigen Phase zurückgehalten werden.

5. Von den nicht zu tarnenden Elementen können bzw. müssen durch Vorextraktion bei Abwesenheit von Amin entfernt werden: *Sc, Seltene Erden, In, Ga, Tl(III), Sn(II), Pb, Zr, Hf, Th, Bi, Nb, Ta, Mn(II), Mn(III)* und *Co* sowie *Al*, wenn nur mit KCN getarnt wird, ferner, wenn sie in grösseren Mengen vorliegen, auch *Zn, Cd, Al, Fe(II)* und *Fe(III)*. *Tl(I)* wird durch die Vorextraktion nicht vollständig entfernt, es muss

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deshalb zu Tl(III) oxydiert werden. Ebenfals quantitativ entfernt werden *Cu* und *Ni* durch die Vorextraktion. — Die Vorextraktion wird zweckmässigerweise zunächst bei pH 9 durchgeführt und dann bei pH 11-11.5 nochmals wiederholt. Sie führt bei den meisten Elementen bei pH 9 schneller zum Ziel, weil ein Teil der Elemente bei pH 11 bereits nicht mehr vollständig in die Chloroformphase übergeht. Andererseits werden einige Elemente, wie *Sc*, die *Seltenen Erden* und *Zr* oberhalb pH 10 schneller entfernt. Bei Gegenwart grosser Mengen Fe ist in manchen Fällen sogar eine Vorextraktion bei pH 5 angebracht. Bei der Vorextraktion dürfen noch keine Komplexbildner ausser Tartrat und H_2O_2 zugegen sein, weil sie dadurch bei einige Elementen unvollständig würde. — Bei sehr grossen Mengen fremder Ionen ist die dann mehrfach durchzuführende Vorextraktion unbequem. Man wird deshalb in solchen Fällen nach Möglichkeit das in grossem Überschuss vorhandene Element vorher auf anderem Wege weitgehend entfernen, z.B. bei der Analyse von Al- oder Zn-Legierungen, wie unten beschrieben, durch Behandlung mit NaOH, oder bei Eisenlegierungen oder -salzen, indem die Hauptmenge Fe durch Ätherextraktion aus 6*N* HCl-Lösung entfernt wird usw. Eine vorherige Entfernung ist erforderlich bei grösseren Mengen *Zr* (>5 mg), *Bi* (>5 mg), *Th* und *Seltener Erden* (>7 mg), weil diese Elemente nur zu einem Teil in die Chloroformphase übergehen und auch durch wiederholte Vorextraktion nur langsam entfernt werden. Zur vorherigen Abtrennung eignet sich für Zr+Bi die Extraktion als Cupferrate mit Chloroform aus 1*M* H_2SO_4 (dabei werden auch eine ganze Reihe anderer Elemente entfernt, so dass diese Vortrennung auch in anderen Fällen angebracht sein kann) und für Th + Seltene Erden die Fällung als Oxalate aus 1*M* salpetersaurer Lösung bei Abwesenheit von Ammonsalzen mit anschliessender Vorextraktion.

6. Die Mitextraktion einiger Elemente lässt sich durch Erhöhung des pH-Wertes bei der Mg-Extraktion verhindern, z.B. von *Zn*, *Cd*, *Zr*, *Hf* und *Al* oberhalb pH 12.5, *Ti* oberhalb pH 13, *V* oberhalb pH 12. In diesen Fällen ist die Chloroformlösung durch Zusatz von Methanol zu stabilisieren.

Insgesamt ergibt sich also, dass die Mg-Bestimmung durch relativ wenige Manipulationen spezifisch gestaltet werden kann. In Tab. IV sind einige quantitative Mg-Bestimmungen (je 120 γ Mg vorgegeben) bei Gegenwart je eines anderen Elementes im Überschuss angeführt. Der Fehler liegt im Mittel bei ± 1.7%; die maximale Abweichung überschreitet in keinem Falle die 5%-Grenze.

VORSCHRIFT ZUR PHOTOMETRISCHEN BESTIMMUNG DES Mg ALS MAGNESIUMOXINAT IN CHLOROFORMLÖSUNG BEI GEGENWART ANDERER ELEMENTE

Reagentien für die Grundoperation:
0.1%ige Lösung von Oxin in Chloroform (= *ca.* 0.007*M*)
1*N* KNa-Tartrat-Lösung
1*N* NH_3-Lösung
n-Butylamin (reinst)
wasserfreies Na_2SO_4 oder Methanol (reinst)
KCN p.a.
Perhydrol (30%ige Lösung von H_2O_2)
Spezialindikatorpapier, pH-Bereich 8-12.

Man wägt eine passende Durchschnittsprobe von 0.5-1 g der Substanz ab, löst in einem geeigneten Lösungsmittel oder schliesst auf, führt zweckmässige oder erforderliche Vortrennungen durch (siehe vorhergehenden Abschnitt) und füllt auf 100 oder 250 ml je nach Mg-Gehalt auf. Einen aliquoten Teil dieser neutralen oder schwach sauren Lösung, der etwa 20-200 γ Mg enthalten soll, gibt man in einen 150 ml Scheidetrichter und setzt 5 ml der 1*N*-Tartratlösung und bei Gegenwart von V, Ti und U je nach deren Menge 1-3 ml Perhydrol zu, verdünnt auf *ca.* 40 ml mit Wasser und neutralisiert mit der 1*N* NH_3-Lösung (*ca.* 4 ml) auf etwa pH 9. (Kontrolle mit Spezialindikatorpapier.)

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Anschliessend schüttelt man einige Male mit *ca.* 20 ml der 0.1%igen Oxin-Chloroformlösung, bis die Lösung farblos bleibt. Bei Anwesenheit sehr grosser Mengen fremder, durch Vorextraktion entfernbarer Elemente kann hier eine höher konzentrierte Oxin-Chloroformlösung (1-3%ig) verwandt werden. Dann gibt man weiteres NH_3 zu der wässrigen Lösung und wiederholt (insbes. bei Gegenwart von Zr, Sc und Seltenen Erden) die Vorextraktion bei pH 10.5-11.5, wobei im allgemeinen eine Ausschüttelung genügt. Anschliessend versetzt man zur Tarnung der verbliebenen Elemente mit 0.5-1 g festem KCN, setzt 1 ml *n*-Butylamin zu, mischt durch kurzes Umschütteln und kontrolliert nochmals den pH-Wert, der 11.0 ± 0.5 betragen soll. Danach wird das Magnesium extrahiert, wobei folgende Varianten offenstehen:

1. Variante: (Chloroformtröpfchen von der Vorextraktion dürfen nicht mehr vorhanden sein!) Man gibt genau abgemessen 50 ml der Oxin-Chloroformlösung zu, schüttelt eine Minute und lässt einen Teil der Chloroformphase in eine Schliffflasche zu einer Spatelspitze Na_2SO_4 fliessen, schüttelt kurz um, lässt absitzen und photometriert die überstehende klare Lösung.

2. Variante: Man gibt 20 ml der Oxin-Chloroformlösung zu, schüttelt *ca.* 30 Sekunden und lässt die Chloroformphase möglichst vollständig in einen 50 ml Messkolben fliessen. Man wiederholt die Extraktion mit weiteren 20 ml Chloroformlösung, vereinigt beide Phasen, gibt 2 ml Methanol zu, füllt auf 50 ml auf und photometriert. Diese Variante *muss* für Extraktionen bei pH > 11.5 angewandt werden.

In beiden Fällen misst man die Extinktion bei 380 mμ oder mit dem entsprechenden Filter (S38E) eines Filterphotometers gegen eine gleich behandelte Reagentienblindlösung.

Die Bestimmung dauert höchstens eine Stunde einschliesslich der Abtrennung störender Elemente, jedoch ohne Berücksichtigung komplizierterer Aufschlüsse oder Vortrennungen durch Fällung und Filtration.

GLEICHZEITIGE BESTIMMUNG KLEINER MENGEN Fe UND Mg

Das Eisenoxinat $FeOx_3$ ist im Gegensatz zu den anderen, meist gelben Metalloxinaten tiefolivbraun bis schwarz gefärbt. Es hat noch bei 580 mμ ein flaches Absorptionsmaximum (molarer dekadischer Extinktionskoeffizient $\varkappa_{580} = 3700$), während die anderen Metalloxinate ausser Vanadin(V) bei dieser Wellenlänge nicht mehr merklich absorbieren. Eine Eisenbestimmung ist deshalb auch bei Anwesenheit mässiger Mengen anderer Oxinate in der Chloroformphase möglich, wie dies für die gleichzeitige photometrische Bestimmung von Eisen und Kupfer im Blutserum bereits beschrieben wurde[9]. In Verbindung mit der Magnesiumbestimmung gestaltet sich die gleichzeitige Eisenbestimmung in den Vorextrakten folgendermassen:

Man führt die Vorextraktion bei pH 9 (oder auch pH 5) mit 20 ml-Portionen der Oxin-Chloroformlösung durch, bis die letzte Fraktion farblos ist. (Bei Gegenwart von V(V) ist vorher H_2O_2 zuzusetzen.) Man vereinigt alle Chloroformfraktionen, füllt auf ein bestimmtes Volumen auf, trocknet mit Na_2SO_4 und misst die Extinktion bei 580 mμ gegen eine entsprechend bereitete Reagentienblindlösung. Den Fe-Gehalt der Lösung entnimmt man einer entsprechend aufgenommen Eichkurve. Das Beer'sche Gesetz ist im Konzentrationsbereich von 0.1-12 γ Fe/ml erfüllt.

ANWENDUNGSBEISPIELE

a) Magnesiumbestimmung in Calciummineralien

Die Proben wurden in Salzsäure gelöst, ohne weitere Vorbehandlung nach Tartratzugabe mit NH_3 auf pH 11 eingestellt und zweimal mit 20 ml der Oxin-Chloroformlösung vorextrahiert. Dann wurde 1 ml Butylamin zugesetzt und nach Variante 1 das Mg bestimmt. In Tab. Va sind die Ergebnisse für drei Mineralien angegeben.

b) Magnesiumbestimmung in Aluminiumlegierungen

Die Metallspäne wurden in Natronlauge gelöst, der Rückstand, der alles Mg und Fe enthielt, abfiltriert, mit verdünnter Natronlauge gewaschen und in Salzsäure gelöst. Bei den beiden Siluminproben (I und III) wurden die Späne in Salzsäure gelöst, der

TABELLE V

BELEGANALYSEN

	Probe	*% MgO[a]*	*gefunden nach Oxinmethode % MgO*
aI	Kreide:[a] 54.3% CaO; 39.4% CO_2; 0,86% SiO_2 0.86% Fe_2O_3/Al_2O_3	0.72—0.80	0.76
aII	Kalkstein:[a] 44.1% CaO; 35.0% CO_2; 16.0% SiO_2; 1.0% Fe_2O_3/Al_2O_3	0.30—0.32	0.28
aIII	Dolomit:[a] 34.3% CaO; 46.5% CO_2; 0.43% Fe_2O_3/Al_2O_3	18.2	18.2

	Probe	*% Fe[b]*	*% Mg[b]*	*% Fe*	*% Mg*
bI	Silumin:[b] 9.95% Si; 0.36% Mn; 0.01% Cu; 0.05% Zn	0.19	0.37	n.b.	0.35
bII	Aluminiumlegierung:[b] 0.92% Si; 0.72% Mn; 0.01% Cu; 0.05% Zn	0.22	0.85	0.23	0.85
bIII	Silumin:[b] 9.87% Si; 0.41% Mn; 0.01% Cu; 0.05% Zn	0.22	0.29	n.b.	0.28
bIV	Aluminiumlegierung:[b] 0.10% Si; 0.01% Cu; 0.05% Zn	0.14	4.08	0.13	3.80
bV	Aluminiumlegierung:[b] 0.46% Si; 0.35% Mn	0.42	0.045	0.40	0.042
c	Zinkmetall: ∼1% sonst. Bestandteile (Cu, Mn)[a]	0.016—0.025[a]	0.024—0.027[a]	0.019	A: 0.031 B: 0.028

[a] Analysen durch unabhängige Bearbeiter und nach anderen Methoden.
[b] Gehalte nach Angaben der Herstellerfirma.

aus Si (und SiO_2) bestehende Rückstand abfiltriert, das Filtrat natronalkalisch gemacht und der Niederschlag wie oben weiter behandelt. Die Lösungen wurden mit Tartrat versetzt, mit NH_3 auf pH 9 eingestellt und je dreimal mit je 20 ml der Oxin-Chloroformlösung vorextrahiert. Diese Lösungen dienten in einigen Fällen zur Fe-Bestimmung (Probe II, IV und V). Dann wurde 1 ml Butylamin zugesetzt und das Mg bei pH 11.3 extrahiert. Die Ergebnisse finden sich in Tab. Vb.

c) Magnesiumbestimmung in Zink

Das Zink wurde in Salzsäure gelöst, die Lösung mit überschüssigem, festen NaOH behandelt, der Niederschlag abfiltriert und wie bei Al weiterbehandelt. In dem Vorextrakt wurde Eisen bestimmt.

Bei Analyse A (Tab. Vc) wurde nach der Vorextraktion direkt, bei Analyse B nach Zusatz einer Spatelspitze KCN das Mg extrahiert. Wie sich bereits bei den Voruntersuchungen ergeben hatte, wird Zn durch die Vorextraktion nicht ganz vollständig

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entfernt, eine zusätzliche Tarnung durch KCN ist also erforderlich, da sonst die Ergebnisse der Mg-Bestimmung etwas zu hoch ausfallen.

In allen Fällen wurden die Vergleichsanalysen nach unabhängigen Methoden (meist gravimetrisch) und von unabhängigen Bearbeitern durchgeführt.

ZUSAMMENFASSUNG

Das Magnesiumoxinat löst sich unter normalen Bedingungen nicht in unpolaren organischen Lösungsmitteln. Bei Gegenwart von 2% Butylamin kann jedoch im pH-Bereich 10.5-13.6 das Mg quantitativ mit einer 0.1%igen Oxin-Chloroformlösung extrahiert und im Konzentrationsbereich 0.05-10 γ Mg/ml durch Messung der Extinktion bei 380 mμ photometrisch bestimmt werden. Diese Reaktion wurde zu einer spezifischen Bestimmungsmethode kleiner Magnesiummengen bei Gegenwart aller wichtigen anderen Elemente ausgearbeitet. Ausserdem kann die Mg-Bestimmung auf einfache Weise mit einer photometrischen Bestimmung kleiner Eisengehalte, ebenfalls als Oxinat, kombiniert werden. Als Beispiel für die praktische Anwendung wurden Magnesium- und Eisenbestimmungen in einigen Ca-Mineralien, Al-Legierungen und einer Zinklegierung durchgeführt.

SUMMARY

Under normal conditions, magnesium oxinate does not dissolve in non-polar organic solvents. In the presence of 2% butyl amine, however, magnesium can be extracted quantitatively in the pH range 10.5-13.6 by a 0.1% oxine-chloroform solution (concentration range 0.05-10 γ Mg/ml), and can be determined photometrically by measurement of the extinction at 380 mμ. This reaction has been elaborated to a specific method of determination for small quantities of magnesium in the presence of the most important other elements. Furthermore, determination of magnesium can be combined quite simply with a photometric determination of slight iron content, also as the oxinate. The practical application of the method is demonstrated by determination of magnesium and iron in several calcium minerals, aluminium alloys and a zinc alloy.

RÉSUMÉ

L'oxinate de magnésium, dans des conditions normales ne se dissout pas dans des solvents organiques non polaires. En présence de butylamine (2%), à un pH 10.5 à 13.6, le magnésium peut cependant être extrait quantitativement au moyen d'une solution d'oxine à 0.1% dans le chloroforme. Le dosage photométrique du magnésium est possible pour des concentrations de 0.05 à 10 γ Mg/ml, par mesure de l'extinction à 380 mμ. Cette réaction permet un dosage spécifique de petites quantités de magnésium en présence de tous les autres éléments importants. En outre, ce dosage du magnésium peut être combiné facilement avec un dosage photométrique de faibles quantités de fer, également sous forme d'oxinate. Comme exemples pratiques, on a appliqué ces dosages de magnésium et de fer à des minerais de calcium, à des alliages d'aluminium et à un alliage de zinc.

LITERATUR

[1] F. Hahn, *Z. angew. Chem.*, 39 (1926) 1198.
[2] R. Berg, *Z. anal. Chem.*, 71 (1927) 23.
[3] R. Berg, *Pharm. Ztg.*, 71 (1926) 1542.
[4] R. Bittel, *Ann. inst. natl. recerche agron.*, A 2 (1951) 144; dort weitere Angaben.
[5] R. Fresenius und G. Jander, *Handbuch der analytischen Chemie*, Springer, Berlin, 1945, Teil III, Bd. IIa, S. 168.
[6] L. L. Merrit jr., *Anal. Chem.*, 25 (1953) 718.
[7] C. L. Luke und Mary E. Campbell, *Anal. Chem.*, 26 (1954) 1778.
[8] F. Umland und W. Hoffmann, *Angew. Chem.*, 68 (1956) 704.
F. Umland und F. G. Weyer, *Klin. Wochschr.*, 33 (1955) 237.

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COULOMETRY APPLIED TO GAS-PHASE CHROMATOGRAPY*

by

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The importance of chromatography in analytical determinations has led to the development of many devices for the identification and quantitative determination of the components eluted through a chromatographic column. Coulometry is an extremely sensitive analytical technique particularly suitable for micro titrations and seems to meet the requirements for a useful detector; it offers many interesting aspects: simplicity of operation, low cost, simple construction, rugged and stable operation.

In the photometric titrations the gas stream from the column bubbles up through a titration cell containing a suitable indicator; the acidic (or basic) vapors alter the pH of the solution in the titration cell, and hence the color of the indicator. By means of a photocell relay this color change is made to operate a burette and to drive a recording pen across a revolving drum. The burette contains alkali (or acid) of an appropriate strength, which is added until the original pH is restored. By using a similar set up and by inserting in the titration cell two generator electrodes, it is possible to perform coulometric titrations of the eluted components of a gas or vaporizable mixture.

The necessary condition for the applicability of coulometry is the presence in the molecule of a compound, which has to be determined, of a functional group which can be quantitatively titrated by a reagent generated by electrolysis; therefore compounds such as volatile acids or bases, mercaptans, aldehydes and ketones etc. may be titrated by coulometry; the use of this procedure needs not be confined, however, only to these compounds, because it might be extended to all organic vapors by burning them at the end of the column and converting them into carbon dioxide which can be coulometrically titrated.

This research has been performed to investigate the applications of coulometric titrations to either manual or automatic gas-chromatograms.

EXPERIMENTAL

A conventional scheme for gas-chromatography, which can be easily built from standard laboratory equipment is shown in Fig. 1. A chromatographic column, which consists of 6 mm internal diameter glass tubing is thermostated in a vapor jacket, fed by a boiling liquid; the elution gas is kept at a constant pressure by a simple manostat and the flow is measured by a rotameter or by a flowmeter. The type of the titration cell, where the elution gas bubbles, changes according to the substances titrated and the procedure used to follow up the titration. Consideration has been given to the use of end-points which imply an electrical signal (photometric, amperometric, potentiometric). This eventually can be amplified and by means of a relay, it can drive a stabilized current supply and a recording pen for automatic titrations.

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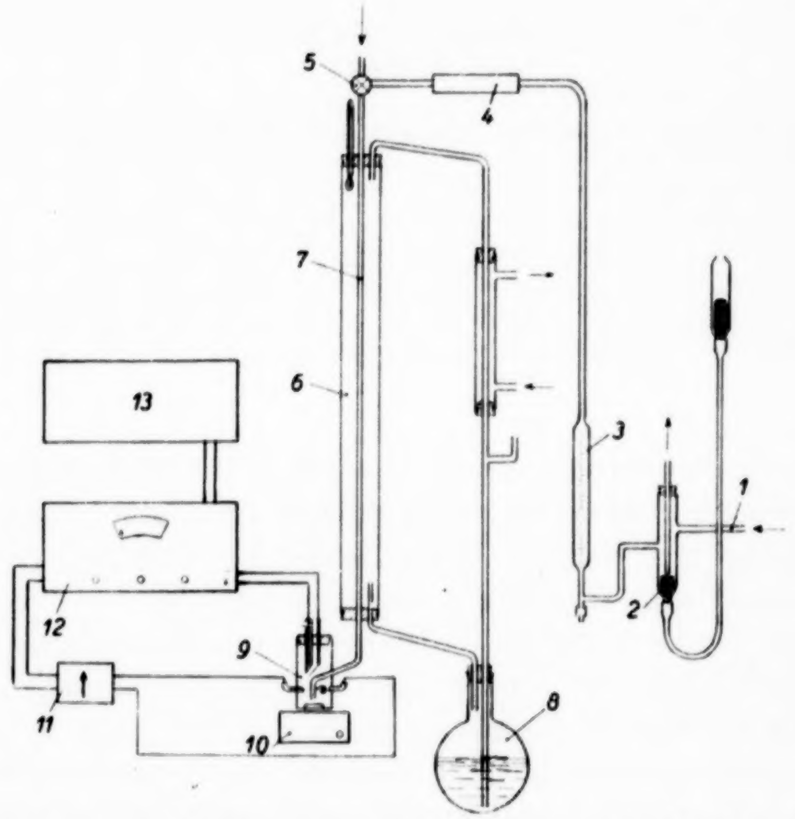

Fig. 1. General set-up for gas-phase chromatography and coulometric titration: 1. Inlet for elution gas; 2. Manostat; 3. Flowmeter; 4. Cartridge for gas purification; 5. Three ways stopcock for sample introduction; 6. Vapour jacket. 7. Chromatographic column; 8. Boiler; 9. Titration cell for potentiometric end-point; 10. Magnetic stirrer; 11. Stopwatch; 12. Coulometer; 13. Recorder.

A constant current supply might be a large capacity battery but a coulometer, especially designed for automatic titrations, has been made.

The microcoulotitrator, which is extensively described elsewhere[1], has the following features:

a) Supply of constant current in the range 0.2-40 mA *i.e.* I = const.

b) Electronic circuit to trigger the constant current supply at a determined signal of the indicator electrodes *i.e.* I = const. and automatic end-point.

c) Electronic device to supply, by means of a servo-system, a current, the intensity of which is proportional to the intensity of the indicator signal (S) *i.e.* $\frac{\mathrm{d}I}{\mathrm{d}t}$ proportional to $\frac{\mathrm{d}S}{\mathrm{d}t}$.

The titrator may be used either for manual or automatic titration.

In the former the operator switches on the current whenever the selected indicator shows a signal and draws a curve "generation time" versus "elution time"; in the latter according to feature b) an electromagnetic stopwatch indicates the time, the constant current electrolysis flows in the titration cells; the stopwatch may be replaced by a recorder.

Since the concentration of a component eluted through the column changes with the time and generally produces a symmetrical elution peak, it may however be desirable to follow the concentration in the time and the possibility given by feature c) is used.

The electrical scheme of the microtitrator is reported in Fig. 2; the power supply (section A-B) is a classical high feed-back circuit which produces a stabilised current ($< 1^0/_{00}$). The trigger is essentially a switch that operates at a selected potential of the indicator electrodes. In any titration it is always possible to have at the end-point a change of potential or a change of current intensity: a general procedure is the use of the combination microammeter-phototube. The two indicator electrodes are connected through a convenient circuit (Fig. 2 section C) to a microammeter; at the base of the needle indicator of this instrument an opaque screen is fixed up; in the front of it is set a stabilized source of light (L) and behind it a phototube (T_{12}); when the indicator electrodes indicate the flow of a current, the needle shifts and the current of the phototube, which is amplified, operates a relay. In order to have a stabilised current, the intensity of which is proportional to the indicator signal a servo-system is used; the control potential V_c is compared with the output potential through a voltage divider R_4R_5. The voltage resulting from the unbalance of the bridge, operates the grid of the tube T_9; the output is proportional to the phototube current and therefore to the position of the needle.

Coulometric titrations of the eluted components may be performed by using photometric, potentiometric and amperometric devices. All methods have been checked for the titration of many substances and some of the cells used are briefly described.

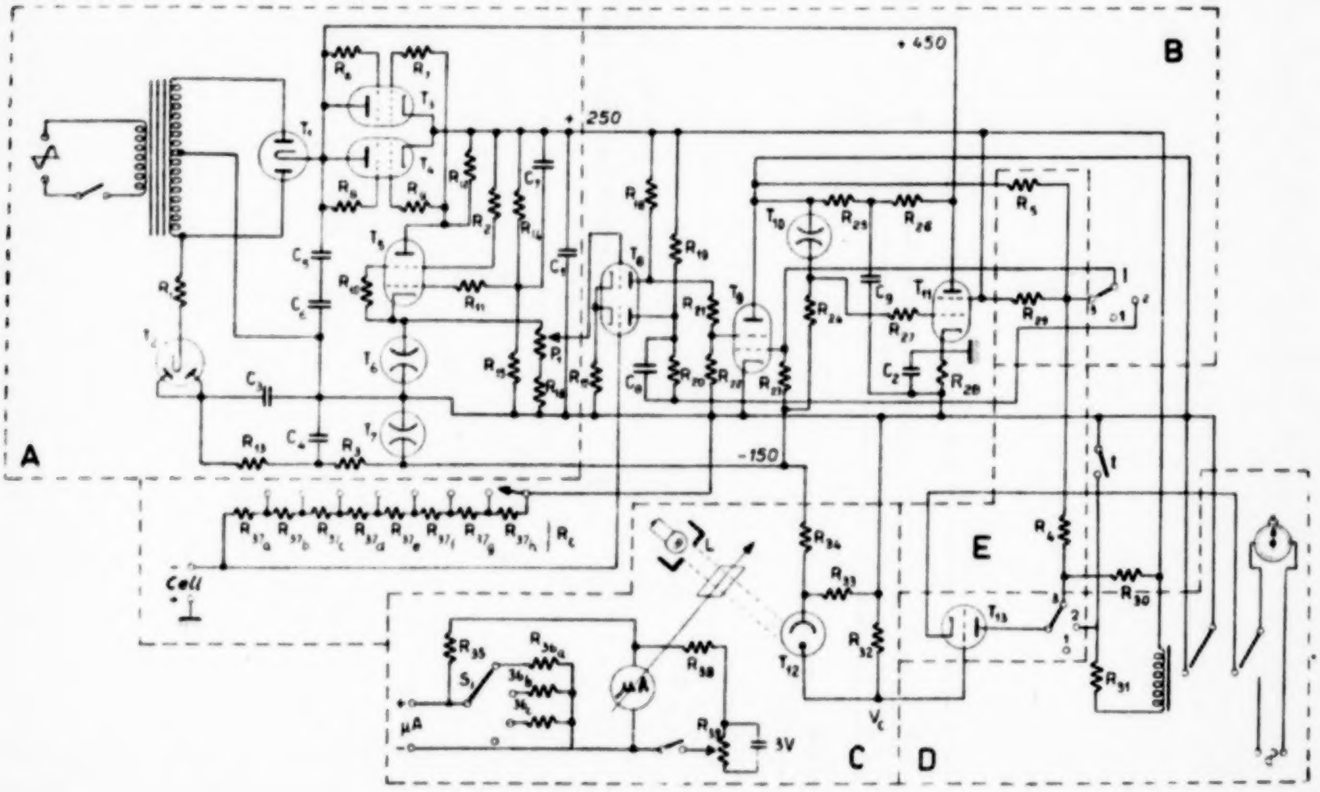

Fig. 2. Electric scheme for millicoulometer:
A: tension stabilizer circuit; B: current stabilizer circuit; C: indicator system; D: trigger. E: servo-system circuit.
$T_1 = 5U4$; $T_2 = 6 \times 5$; $T_3 = T_4 = T_{11} = 6L6$; $T_6 = 85A2$; $T_7 = T_{10} = CV104$; $T_8 = 6SL7$; $T_9 = 6SH7$; $T_{12} = 918$; $T_{13} = 1/3\ 6SN7$.

Photometric end-point

A perspex cell (25 × 25 × 65 mm) is used which contains a solution 0.5*M* is Na_2SO_4 as absorbing solution and the chosen indicator. The generating electrode is a rotating platinum electrode with a platinum sheet helix-shaped (about 40 mm^2) to perform the mixing of the solution.

In order to have a sharp color change of the indicator and to render the detection system sensitive to color and independent of changes of optical density due to bubbles of various origin, a differential photometric system has been used by employing two selenium photocells set in opposition: one of them is covered with an interferential optical filter, which has a transmission band corresponding to the absorption maximum of the chosen indicator and the surface of the other, uncovered, may be regulated. Anodic or cathodic compartments can be connected by a salt bridge or by a collodion membrane.

This arrangement has been used for the titration of mixtures of organic acids. A typical gas-phase chromatogram of a mixture of formic, acetic, propionic, butyric and isovaleric acid is reported in Fig. 3. The titration was performed by coulometry by using a servo-system to obtain a current, the intensity of which is proportional to the intensity of the indicator signal. A Leeds and Northrup Speedomax was used for the registration.

In order to evaluate the accuracy of the titration, different samples of the same mixture were chromatographed and the ratio of the areas of the peaks determined; the following values have been obtained:

Ratio of peaks areas		
$\frac{A_p}{A_a}$	$\frac{A_p}{A_b}$	$\frac{A_b}{A_a}$
1.15	2.89	0.403
1.13	2.89	0.413
1.11	2.86	0.398

where: A_a = peak area for acetic acid
A_b = ,, ,, ,, butyric acid
A_p = ,, ,, ,, propionic acid

The constancy of the ratio may be considered satisfactory.

The titration can be performed at a constant current but the speed of the recorder is quite critical to prevent overlapping of the squares which indicate the time of reagent generation.

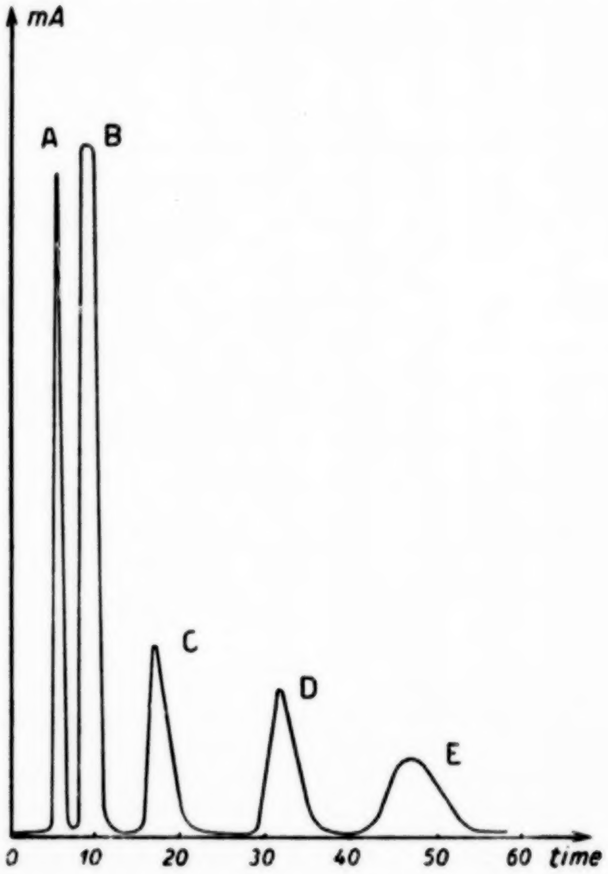

Fig. 3. Gas-chromatogram of a mixture of fatty acids. A formic, B acetic, C propionic, D butyric, E *iso*-valeric acids.
Column: 1 m, 5 mm diam.; liquid phase: stearic acid (10% w/w) in D.C. 550 silicone, temp. 100°C; flow rate 30 ml/min.

Potentiometric end-point

The cell reported in Fig. 4 has been found to be very effective and very convenient for the titration of carbon dioxide and volatile acids; it has been arranged from the cell devised by **Oelsen** *et al.*[2]. It consists of a glass cylinder of 12 cm height and 2.5 cm internal diameter; in its lower part two holes are made to insert the indicator electrode (a platinum wire, 1 mm section, disc-shaped) and a *N* calomel electrode as a reference: above them through a third hole the cell is connected to the chromatographic column. The gas bubbles into the cell through a fritted gas disc.

The electrolyte solution contains 10 g $BaCl_2 \cdot 2H_2O$, 5 ml ethanol and 0.5 ml 35% H_2O_2 per liter and is rendered slightly alkaline (pH = 9.8) either by addition of dilute alkali or by generation of hydroxyl-ions. It has been shown[3] that a platinum sheet in a stirred dilute solution of hydrogen peroxide is a mixed electrode which may be called "hydrogen peroxide electrode" and which behaves as a hydrogen ion indicator. When the pH of the solution is about 9.8, the potential difference between the two electrodes is equal to zero: as soon as the pH changes by the introduction of carbon dioxide or any acidic substance the microammeter connected to the indicator and the *N* calomel electrode shows the flow of a current. By generation of OH^- the potential difference is brought back again to zero. This cell may be used for the direct titration of CO_2 and volatile acids and also for the titration of any organic vapor. In the latter case a small furnace filled up with copper oxide and kept at about 700°C is set at the end of the chromatographic column; the vapor is burnt to carbon dioxide which is transferred by the elution gas to the cell where it is continuously titrated. The OH^- generation takes place at the electrode (7), which consists of a platinum sheet. The anode, made of a cylinder of carbon, is separated by a collodion membrane; a solution of 0.5M sodium sulphate is made to circulate slowly in the anodic compartment.

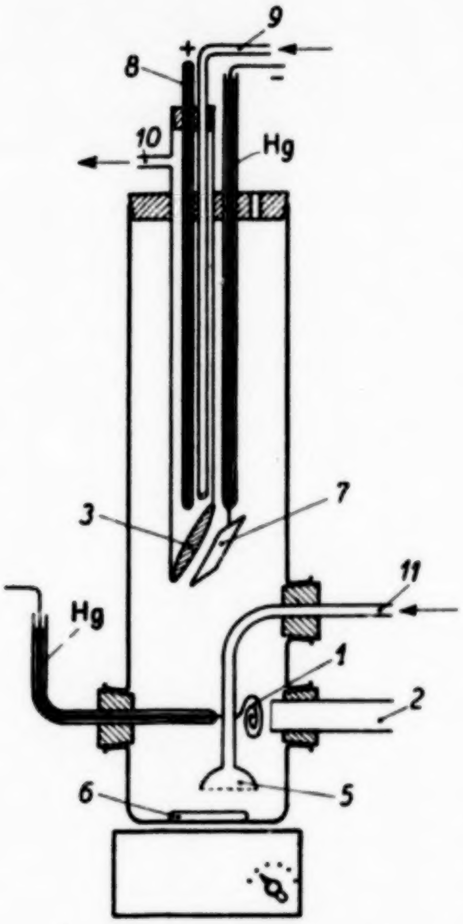

Fig. 4. Titration cell for CO$_2$ and acid vapors.
1. Platinum wire, 2. N potassium chloride bridge connected to N calomel electrode, 3. collodion membrane; 5. fritted glass; 6. magnetic stirrer; 7. generator cathode: platinum sheet; 8. generator anode: carbon electrode, 9-10. inlet and outlet for the flowing anodic solution; 11. inlet-elution gas.

A manual gas-phase chromatogram of a mixture of organic acids titrated as such is shown in Fig. 5; it can be obtained as well after combustion of the eluted components to carbon dioxide and performed automatically by employing the servo-system described.

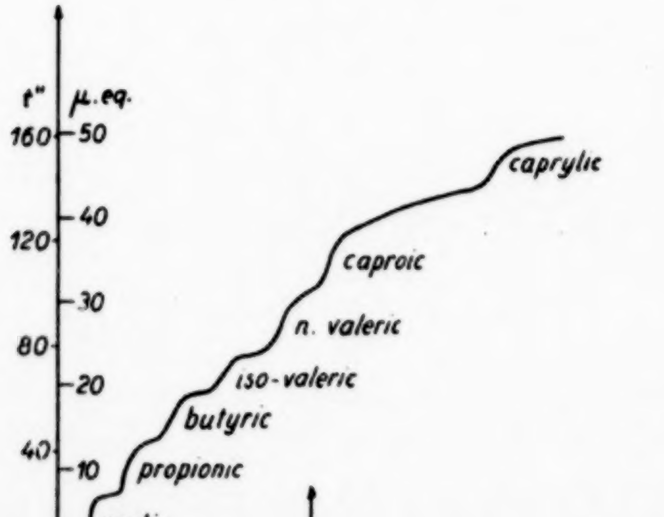

Fig. 5. Gas phase chromatogram of organic acids by manual coulometric titration.

Gas-chromatograms of many substances can be realised by this device; the procedure is extremely simple and there is no limitation to its use as far as the working temperature of the column is concerned. It is only necessary that the components to be determined have at least one carbon atom in their molecule.

Amperometric end-point

It has been successfully applied to the titration of mercaptans separated as suggested by S. SUNNER *et al.*[4] in a chromatographic column packed either with carborundum and using dioctyl phthalate containing 5% diphenylamine as the liquid phase or with celite and D.C. silicone as the liquid phase.

The titration cell is similar to the one described in the preceding paragraph. In the holes at the lower part of the cell are inserted a silver wire, as a generating electrode, and a potassium nitrate bridge connected with a platinum cathode. The electrolyte solution is 0.5*M* KNO_3 in ethanol 70%; it contains a trace of gelatine (0.1%) and a definite concentration of silver ions; the indicator electrode is a rotating platinum electrode which, together with the reference electrode is short-circuited on the microammeter. This instrument is either mechanically or electrically set to zero. The mercaptans flowing out of the column react quantitatively with silver ions and by means of the electronic servo-system the silver concentration is brought to the initial value.

A gas-chromatogram of a mixture of mercaptans is shown in Fig. 6; in Table I the results of several gas-chromatograms of mercaptans mixtures are reported.

TABLE I

	A		*B*		*C*	
	present	*recovered*	*present*	*recovered*	*present*	*recovered*
iso-Propyl — SH (μeq)	6.15	6.13	4.78	4.78	6.62	5.32
n-Propyl — SH (μeq)	10.0	10.2	7.70	7.80	10.29	9.95
iso-Butyl — SH (μeq)	11.62	11.47	8.90	8.44	11.8	11.8
n-Butyl — SH (μeq)	8.89	8.49	6.82	6.89	9.05	9.06
Amyl — — SH (μeq)	8.42	8.23	—	—	8.68	8.28

CONCLUSION

The coulometric titration of components separated in gas phase chromatography can be successfully performed.

The separation and the titration of the following classes of substances has been achieved (see Table II).

TABLE II

Substances	*Reagent*	*Procedure*	*Absorbing solution*
Acids	OH^-	photometric end-point	0.5*M* Na_2SO_4
Acid -CO_2	OH^-	potentiometric end-point	$BaCl_2$-H_2O_2-C_2H_5OH
Bases	H^+	photometric end-point	0.5*M* Na_2SO_4
Mercaptans	Ag^+	amperometric end-point	70% ethanol - 0.5*M* KNO_3
Aldehydes and ketones	OH^-	photometric end-point	0.2*M* $NH_2OH.HCl$

The use of a furnace at the end of the column which burns up the single components and converts them into carbon dioxide, permits the determination of any organic vaporizable substance. This fact is of great importance because this technique might be used in connection with chromatographic separations obtained at a fairly high temperature where other physical methods may present objections and limitations.

Another interesting feature of this technique is the possibility of titrating only one class of substances in the presence of many others which may interfere in the chromatographic separation.

A general advantage is the high degree of accuracy which can be obtained by coulometry in the titration of components on a micro scale.

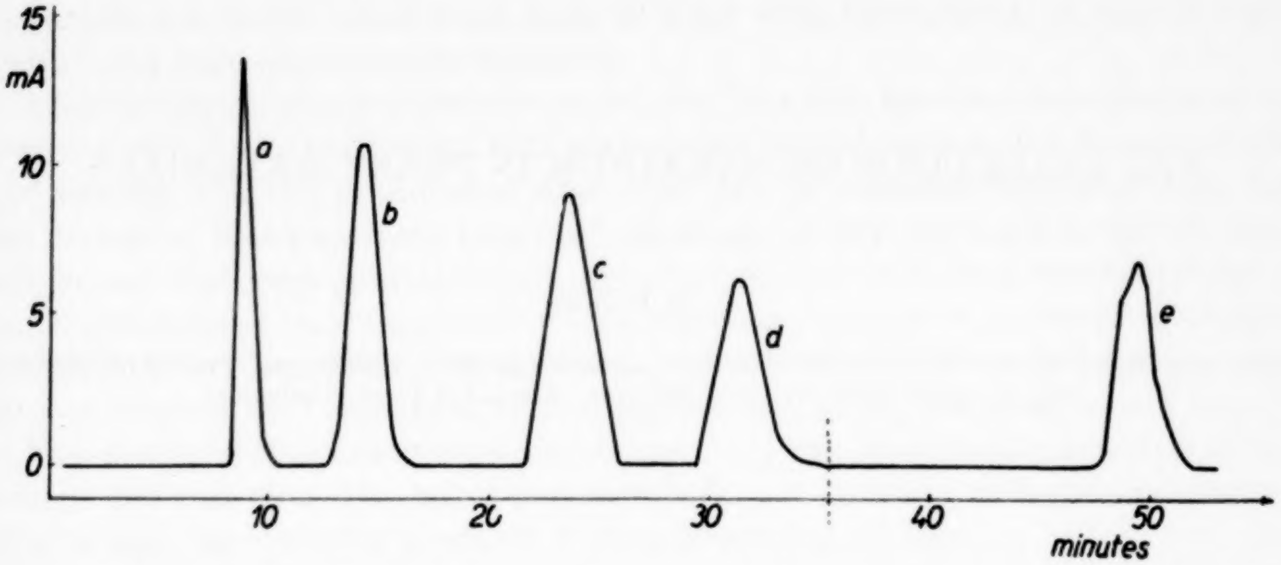

Fig. 6. Gas-phase chromatogram of a mixture of mercaptans: a. *iso*-propyl; b. *n*-propyl; c. *iso*-butyl; d. *n*-butyl; e. *n*-amyl; T = 78°C; flow rate: 20 ml/min-40 ml/min.

SUMMARY

It has been found that coulometry is an excellent procedure for identification and quantitative determination of the components of an organic mixture, separated by vapor-phase chromatography. A millicoulometer is described which can be used either for manual or automatic titration. The eluted components are absorbed in a suitable solution where they are continuously titrated by an electrolytically generated reagent. Photometric, amperometric and potentiometric end-points may be used for the titration of compounds with an active functional group such as volatile acids, bases, mercaptans and aldehydes. The procedure can be extended to all organic vapors by burning them at the end of the column and converting them into carbon dioxide which can be coulometrically titrated.

RÉSUMÉ

La coulométrie constitue une excellente méthode pour l'identification et le dosage des composants d'un mélange organique, séparés par chromatographie en phase gazeuse. Un millicoulomètre est décrit pouvant être utilisé pour de simples titrages et aussi pour des titrages automatiques. Les composés élués sont absorbés dans une solution appropriée et titrés coulométriquement, par le réactif électrolytiquement produit. On peut utiliser la photométrie, l'ampérométrie et la potentiométrie, l'ampérométrie et la potentiométrie pour déterminer le point final lors des titrages de composés renfermant une fonction active, tels que des bases, des mercaptans, des aldéhydes et des acides volatils. Ce procédé peut être appliqué à toutes les vapeurs organiques, en les brulant à l'extrémité de la colonne chromatographique et en les transformant ainsi en anhydride carbonique pouvant être titré coulométriquement.

ZUSAMMENFASSUNG

Es wurde festgestellt, dass die Coulometrie ein ausgezeichnetes Verfahren zur Identifizierung und quantitativen Bestimmung der Komponenten eines organischen Gemisches, welches durch Gasphasen-Chromatographie getrennt ist, darstellt. Ein Millicoulometer wird beschrieben, welches entweder für Hand- oder automatische Titration verwendet werden kann. Die eluierten Komponenten werden in einer geeigneten Lösung absorbiert, wo sie kontinuierlich mit einem elektrolytisch gebildeten Reagenz titriert werden. Photometrische, amperometrische und potentiometrische Endpunktsbestimmungen können zur Titration von Verbindungen mit einer aktiven funktionellen Gruppe, wie flüchtige Säuren, Basen, Merkaptane und Aldehyde, benutzt werden. Das Verfahren kann für alle organischen Dämpfe angewendet werden, indem diese am Ende der Säule verbrannt und in Kohlendioxyd umgewandelt werden, welches coulometrisch titriert wird.

REFERENCES

[1] A. Liberti, F. Lepri, L. Ciavatta and G. P. Cartoni, *Contributi Teorici e Sperimentali di Polarografia*, Cons. Naz. Richerche Roma, 1957.
[2] W. Oelsen, H. Haase and G. Graue, *Arch. Eisenhüttenw.*, 22(1951) 225.
[3] A. Liberti and G. P. Cartoni, *Rend. accad. naz. Lincei*, 20 (1956) 787.
[4] S. Sunner, K. J. Karrman and V. Sunden, *Mikrochim. Acta*, (1956) 1144.

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THE ESTIMATION OF VANADIUM IN PLANT MATERIALS

by

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INTRODUCTION

Until recently there has been little call for a very sensitive quantitative test for microgram to submicrogram quantities of vanadium in plant materials. During the last few years considerable attention has been focussed on the question of whether vanadium is an essential element for plant growth. ARNON AND WESSEL[1] in 1953 noted that with the addition of this metal to nutrient cultures there was an increase in the growth of *Scenedesmus obliquans*.

The classical colorimetric methods, in which hydrogen peroxide or 8-hydroxyquinoline are employed, are not specific in the estimation of vanadium in plant materials, and suffer interference by titanium and molybdenum. The phospho-vanado tungstic acid method is not sufficiently sensitive for quantities less than 5 μg of vanadium, while the concentration by extraction of the complex into a solvent phase is not entirely satisfactory. More recently a method employing benzhydroxamic acid, developed by DAS GUPTA AND SINGH[2] and advanced by WISE AND BRANDT[3], has shown promise, but the latter authors found the lower limit for adherence to Beer's law to be 5×10^{-7} mole (25 μg) of vanadium. The polarograph provides a very sensitive method for the estimation of vanadium, utilising the three-electron reduction wave in a supporting electrolyte composed of ammonia-ammonium chloride, in which concentrations as low as 0.01 μg vanadium per ml may be measured. However, in order to achieve this sensitivity, it is essential that manganese, iron, titanium, aluminium and chromium be completely removed, since the precipitation of the hydroxides of these metals in the alkaline solution invariably leads to the adsorption of some or all of the vanadium present.

One of the greatest difficulties in this estimation is caused by the similarity in the chemical properties of the ferric and the vanadyl ions, and before any method can be really sensitive, the separation of these two metals must be complete. The method of BERTRAND[4], in which iron is precipitated with ammonia in the presence of hydrogen peroxide, was found to be satisfactory on a milligram basis but not on a microgram basis. Attempts to accomplish a chemical separation of vanadium from iron have involved sequestration by versene, cyanide, thiocyanate, fluoride and citrate and the use of anion exchange resins. In all cases, the reaction conditions or the concentrations necessary to completely suppress the extraction of iron, were such that either the vanadium was in the wrong ionic state to react with extractants, or the extraction of the vanadium was seriously impaired.

After the failure of many attempts to accomplish a suitable chemical separation from iron, the adoption of electrolysis with the mercury cathode appeared to be unavoidable, and although this step is somewhat slow, it permits the complete removal of iron. From the review by MAXWELL AND GRAHAM[5] of the use of mercury cathode electrolysis, it will be seen that copper and chromium are also removed. Following the electrolysis, the important metals remaining in solution are vanadium, aluminium, manganese, titanium, molybdenum and tungsten. Manganese and aluminium remain in the aqueous phase after extraction with cupferron, while titanium may be separated by extracting with sodium diethyl dithiocarbamate which at this stage only reacts with vanadium, molybdenum and tungsten. The latter two metals do not interfere with the polarography of vanadium since neither produces a wave in alkaline solution.

EXPERIMENTAL

The conditions suitable for the solvent extraction of vanadium by means of cupferron have been thoroughly investigated by FURMAN, MASON AND PEKOLA[6], but the extent of extractability by sodium diethyl dithiocarbamate over a wide range of pH does not appear to have been previously studied in detail, although BODE[7] examined it from pH 5 to pH 11. An investigation over a wider range was carried out as follows:

Solutions (10%) of ammonium acetate and ammonium tartrate were purified by extracting with 8-hydroxyquinoline and chloroform and then washed thoroughly with chloroform to remove all traces of free oxine. To a series of test solutions each containing 100 μg of vanadium were added 3 ml of the ammonium acetate solution, and the reaction was adjusted by means of sulphuric acid, acetic acid, ammonia or sodium hydroxide to each integral pH value from 1 to 11. A solution (2%) of DDC was prepared and any heavy metal impurities were removed by extraction with chloroform. After the addition of 10 ml of the DDC solution to each of the test solutions, the vanadium complex was extracted with three 5 ml portions of chloroform. The solvent phases were collected in pyrex test tubes from which the chloroform was distilled and the organic residues were digested with concentrated sulphuric and nitric acids.

Since the quantity of vanadium present with complete extraction was 100 μg, the phosphovanado tungstic acid colorimetric method was used for the estimation in this part of the investigation. The procedure followed was that described by SANDELL[8] with a final volume of 10 ml of solution. The colour densities were measured at 400 mμ and expressed as percentages of that of 100 μg of vanadium which had not been put through the extraction process.

The whole process was repeated using ammonium tartrate in place of ammonium acetate. The percentage extraction was plotted against pH value and the results are illustrated in Fig. 1. It will be noted that in the presence of acetate complete extraction is possible with excess DDC between pH 2 and pH 5.5, whereas in the presence of tartrate the range of complete extractability is reduced to between pH 4 and pH 5.

For the polarography of vanadium a number of supporitng electrolytes have been used. LINGANE AND MEITES[9] used 0.1M sodium hydroxide in which the anodic wave of $V^{+4} \rightarrow V^{+5}$ oxidation was measured. The oxalate solution of LINGANE AND MEITES[10] is useful but it only measures the $V^{+4} \rightarrow V^{+2}$ reduction. The most sensitive wave is the doublet of $V^{+5} \rightarrow V^{+4}$ coupled with the $V^{+4} \rightarrow V^{+2}$, which in a strongly ammoniacal solution, appears as a combined three-electron wave, the first step of which is irreversible but the second step is reversible. VON STACKELBERG *et al.*[11] developed the supporting electrolyte $6M$ NH_4OH-$1M$ NH_4Cl, and PAGE AND ROBINSON[12] utilised it for the determination of vanadium in organo-vanadium compounds.

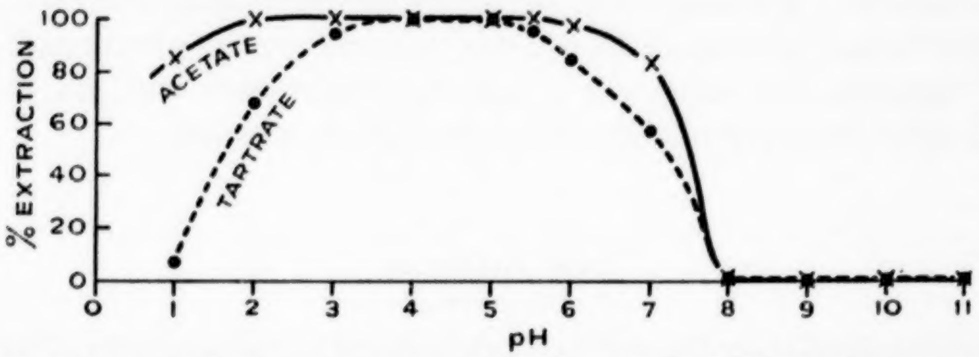

Fig. 1. Showing the extractability of vanadium by sodium diethyl dithiocarbamate in the presence of acetate and tartrate, as influenced by pH.

In the present investigation it was found that $6M$ NH_4OH-$3M$ NH_4Cl produces a wave 20 per cent higher than that given by VON STACKELBERG's electrolyte. A solution containing $6M$ NH_4OH-$3M$ NH_4ClO_4 gives an excellent wave, but on account of the relatively low solubility of NH_4ClO_4, and of the difficulty of removing the last traces of dissolved oxygen from the perchlorate solution, the ammonia-ammonium chloride electrolyte was preferred. This electrolyte is constituted by dissolving the extracted vanadium in 0.5 ml of warm $6M$ hydrochloric acid, and then adding 2.5 ml of $9M$ NH_4OH-$2M$ NH_4Cl. With a final volume of 3 ml the composition becomes $6.5M$ NH_4OH-$3M$ NH_4Cl. Between 5 and 8 molar, the concentration of NH_4OH has little effect on the wave height, but the concentration of NH_4Cl is important. No gelatin was added to this electrolyte as no maxima developed with concentrations lower than 10 μg of vanadium per ml.

The anhydrous vanadyl sulphate obtained after the sulphuric acid has been fumed off, dissolves readily in the warm $6M$ HCl, yet reduction of the vanadium to the tetravalent state does not occur, as is the case when V^{+5} is warmed with concentrated $12M$ hydrochloric acid.

The half wave potential of the vanadium wave in the $6M$ NH_4OH-$3M$ NH_4Cl is —1.30 volts *v.* S.C.E. and — 1.05 volts *v.* the anode pool. By raising the mercury reservoir, the drop time was reduced from 2.4 sec to 1.4 sec, with the result that the height of the wave was almost doubled. The sensitivity of the method might be increased even further by employing drop times as short as 1 second. For very low concentrations of vanadium the polarograph was used as a manual instrument with a minimum of damping, and the results were plotted on graph paper. By allowing the current to reach equilibrium at each value of the applied voltage, at the maximum sensitivity of the polarograph, concentrations as low as 0.01 μg of vanadium per ml of electrolyte could be measured.

APPARATUS

Sargent polarograph model XXI, Heyrovsky cells, and micro cells with mercury pool anodes. Drop time of dropping mercury electrode = 1.4 sec.

Mercury cathode electrolysis cell fitted with a propeller stirrer at the level of the mercury interface.

REAGENTS

Standard vanadium solution. 0.01 M ammonium meta-vanadate solution is prepared and its strength is checked by a permanganate titration following reduction by sulphur dioxide. 0.01 M solution contains 510 µg V per ml, and standard solutions are prepared containing 50 and 5 µg V per ml.

Nitric, sulphuric and perchloric acids purified by distillation. Ammonium acetate 10% solution, purified by extraction with 8-hydroxyquinoline and $CHCl_3$ and washed thoroughly with chloroform to remove the excess oxine.

Cupferron — sublimed, 1% aqueous solution stored in a refrigerator for not more than one week. Sodium diethyl dithiocarbamate (DDC) 2% aqueous solution, filtered, and extracted with chloroform to remove heavy metal impurities. Ammonium hydroxide concentrated, prepared by absorbing gaseous ammonia in glass-distilled water.

Bromocresol green indicator — 0.1% solution in glass-distilled ethanol.

Hydrochloric acid — distilled, constant boiling 6M.

Ammonia-ammonium chloride — 9M NH_4OH-2M NH_4Cl solution prepared without the addition of any gelatin.

PROCEDURE

A 5 g sample of material is digested with nitric and perchloric acids with 5 ml of concentrated sulphuric acid. The volume is made up to 50 ml with water, and after filtration or centrifugation to remove insoluble matter, the solution is transferred to a Melaven electrolysis cell in which the mercury pool is made the cathode. Electrolysis, with 6 volts applied, is continued for 30 minutes.

The important metals removed from the solution at this stage are iron, copper, chromium, and zinc, while V^{+5} is reduced to V^{+4}. Bromine water is added to oxidise the vanadium back to the pentavalent state, and the excess bromine is removed by boiling, after which the solution is filtered to remove any traces of metallic mercury and chromic oxide. In a separating funnel the solution is extracted to exhaustion with cupferron and chloroform. The metals extracted into the solvent phase during this operation are vanadium, titanium, molybdenum and tungsten. Manganese remains in the aqueous phase. The solvent phase is collected in a pyrex test tube from which the chloroform is distilled, and the organic residue is completely oxidised with nitric acid and 10 drops of sulphuric acid.

The inorganic residue in the test tube is transferred to a separating funnel together with 3 ml of ammonium acetate solution and two drops of bromocresol green indicator. Dilute ammonia solution is added until the intermediate green colour of the indicator is reached (pH 4.5-5.0). This solution is now extracted to exhaustion with DDC and chloroform. As with the cupferron extract the chloroform is evaporated, and the residue is decomposed. Since titanium does not react with DDC it remains in the aqueous phase, so that the only important metals extracted into the solvent phase are vanadium, molybdenum and tungsten. The solution of these metallic salts is transferred with rinsings to a small beaker from which the water is evaporated. The sulphuric acid is then fumed off. Two drops of hydrogen peroxide are added and evaporated to dryness, to ensure that the vanadium is completely oxidised to the pentavalent state.

Hydrochloric acid (6M), 0.5 ml, is added with warming in order to dissolve the anhydrous vanadyl sulphate. After cooling, 2.5 ml of 9M NH_4OH-2M NH_4Cl solution is added together with 0.05 g of anhydrous sodium sulphite. The solution is allowed to stand for 10 minutes before being transferred to a polarographic cell. The diffusion current is measured between —0.6 and —1.3 volts *v.* the anode pool. Allowance must be made for the residual current of the supporting electrolyte, particularly at high sensitivities of the polarograph, and it may be incorporated in the reagent blank.

For very small quantities of vanadium, the volume of 6M hydrochloric acid is reduced to 0.1 ml, the 9M NH_4OH-2M NH_4Cl is reduced to 0.5 ml and the 0.6 ml of supporting electrolyte is transferred to a micro-cell by means of a syringe pipette. This permits the estimation of as little as 0.006 µg of vanadium.

A standard curve is prepared by evaporating measured volumes of standard vanadium solution to dryness in small beakers, dissolving the residues in 0.5 ml of 6M hydrochloric acid and 2.5 ml of 9M NH_4OH-2M NH_4Cl and polarographing in the manner described above.

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DISCUSSION

In the above procedure for the estimation of vanadium simplicity has been sacrified for reliability and sensitivity. As a rule polarography provides a considerable degree of specificity but in this case limitations imposed by the alkalinity of the supporting electrolyte, essential to provide the conditions in which the three-electron wave develops, are such as to render necessary a complete separation of vanadium from certain other metals. To attain the desired specificity when determining vanadium in plant materials, the rather long chemical separation is not a particularly great price. Recoveries of added vanadium are 90-95 per cent.

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SUMMARY

A method has been proposed whereby microgram quantities of vanadium may be determined in plant materials. The procedure involves the removal of iron by means of a mercury cathode electrolysis, and the separation of manganese with cupferron and titanium with sodium diethyl dithiocarbamate. The final estimation is made with a polarograph whereby quantities of vanadium down to 0.006 μg may be measured. Although the process involves several steps, it eliminates all of the interfering metals and achieves considerable sensitivity.

RÉSUMÉ

Une méthode est proposée pour le dosage de microquantités de vanadium dans les plantes. Ce procédé comprend l'élimination du fer par électrolyse, avec cathode de mercure, et la séparation du manganèse au moyen du cupferron et du titane au moyen du diéthyldithiocarbamate de sodium. Le dosage final est effectué à l'aide d'un polarographe permettant de mesurer jusqu'à 0.006 μg de vanadium. Bien que cette méthode nécessite plusieurs opérations, elle permet d'éliminer tous les éléments gênants et elle présente une grande sensibilité.

ZUSAMMENFASSUNG

Eine Methode wurde vorgeschlagen, welche erlaubt Mikrogramm-Mengen von Vanadin in pflanzlichen Materialien zu bestimmen. Das Verfahren umfasst die Abtrennung des Eisens durch Quecksilberkathode-Elektrolyse und die Abscheidung von Mangan mit Kupferron und Titan mit Natriumdiäthyldithiokarbamat. Die endgültige Bestimmung erfolgt mit einem Polarographen, wobei Vanadinmengen bis zu 0.006 μg gemessen werden können. Obwohl der Prozess verschiedene Stufen umfasst, eliminiert er alle störenden Metalle und erreicht eine beträchtliche Empfindlichkeit.

REFERENCES

[1] D. I. ARNON AND G. WESSEL, *Nature*, 172 (1953) 1039.
[2] A. K. DAS GUPTA AND M. M. SINGH, *J. Sci. Ind. Research (India)*, 11B (1952) 268.
[3] W. M. WISE AND W. W. BRANDT, *Anal. Chem.*, 27 (1955) 1392.
[4] D. BERTRAND, *Chem. Zentr.*, (1942) II, 1273.
[5] J. A. MAXWELL AND R. P. GRAHAM, *Chem. Revs.*, 46 (1950) 471.
[6] N. H. FURMAN, W. B. MASON AND J. S. PEKOLA, *Anal. Chem.*, 21 (1949) 1325.
[7] H. BODE, *Z. anal. Chem.*, 143 (1954) 182.
[8] E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1944, p. 442.
[9] J. J. LINGANE AND L. MEITES, *Anal. Chem.*, 19 (1947) 159.
[10] J. J. LINGANE AND L. MEITES, *J. Am. Chem. Soc.*, 69 (1947) 1021.
[11] M. v. STACKELBERG, P. KLINGER, W. KOCK AND E. KRATH, *Tech. Mitt. Krupp*, 2 (1939) 59.
[12] J. E. PAGE AND F. E. ROBINSON, *Analyst*, 68 (1943) 269.

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ION EXCHANGE SEPARATIONS IN THE ANALYSIS OF BISMUTH BASE ALLOYS

PART I. BINARY ALLOYS WITH URANIUM AND THORIUM

by

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INTRODUCTION

In the course of work on the study of the solubility of uranium and thorium in metallic bismuth, a need arose for the determination of uranium contents ranging from 50 p.p.m. to 10% and of thorium contents from 0.05 to 10% in binary alloy systems. Some preliminary separation of the bismuth proved necessary before the uranium and thorium determination could be carried out, and of the methods of separation available only ion-exchange seemed to offer a satisfactory solution to the problem. A most valuable contribution by KRAUS AND NELSON[1] is available on ion-exchange behaviour; they reported on the anion exchange properties of many elements in chloride media. The information in this paper indicated distinct possibilities for the separation of bismuth from both uranium and thorium. The absorption of bismuth from hydrochloric acid solutions by an anion exchange resin of the strongly basic quaternary ammonium type is high at low acidity, but decreases with increasing acid strength; it is still fairly high, however, from concentrated hydrochloric acid solutions. In contrast, uranium is not absorbed from weakly acid solutions, slightly absorbed from 2-3M hydrochloric acid solutions and strongly from concentrated acid solutions. The absorption of uranium reaches a maximum from solutions about 9M in hydrochloric acid. Thorium is not absorbed from any hydrochloric acid solutions in the range from 0.05-10M. From this, therefore, it should be possible to effect the quantitative separation of bismuth from uranium and thorium.

The determination of the uranium and thorium concentrations following the ion-exchange separation was not expected to present any particular difficulty. The wide range of uranium and thorium contents of the samples, however, made it necessary to consider the use of two methods of determination for each element. For the higher range of thorium, titration with ethylenediaminetetraacetic acid using pyrocatechol violet[2] as indicator was investigated, but for the lower range the thoronol absorptiometric method was considered to be more suitable[3]. Previous experience with the lead reductor method for uranium[4,5] indicated that this method should serve for all except very low uranium concentrations. The new thoronol method for microgram amounts of uranium after reduction by the lead reductor[6] should be more suitable for the very low uranium contents. Suitable procedures based on the above proposals have been developed and full details of the experimental work are included in this paper.

EXPERIMENTAL

Before investigating the separation of bismuth from uranium and thorium, the solubility of bismuth in hydrochloric acid was briefly studied, and also the capacity of the British resin, Deacidite FF, for bismuth under the optimum conditions of acidity. It was found that 500 mg of bismuth could be held in solution in 50 ml of 10% v/v hydrochloric acid and that this amount of bismuth could be absorbed on to a column of 5 g of air dried resin in a 25 ml burette if passed through the column at a flow rate of not more than 2 ml per minute. To provide a safety factor in subsequent experimental work, the amount of air dried resin necessary was determined by allowing 1 g of resin for each 100 mg of sample and then an extra 2 g of resin. Under such conditions no difficulties were encountered from bismuth passing through the column.

The resin was prepared for use by air drying the commercially available material at 40°C and then grinding it to pass a 40 mesh British Standard sieve. The resulting material was then stirred with water and after allowing a 2-3 min settling time, the water was removed by decantation. This process was repeated two or three times and served to remove unwanted 'fines' from the material. The resin was washed successively with the following solutions: 50% v/v hydrochloric acid, water, cold 10% w/v sodium hydroxide, water, molar nitric acid, 10% v/v hydrochloric acid and finally water. The resulting resin was finally air dried at about 40°C and reserved for use. In preparing the columns, the requisite amount of the resin was weighed out and slurried with water. The slurry was then poured into a 25 ml burette already half full of water and containing a small cotton wool plug for the resin to rest on. The resin was allowed to settle under its own weight with the water flowing slowly out of the burette and before use, the column was washed with 50% v/v hydrochloric acid followed by a 10% v/v solution of the same acid.

The separation and determination of thorium in the presence of bismuth

For the study of the separation of thorium from bismuth, synthetic mixtures were prepared from suitable standard solutions of bismuth and thorium. The thorium solution was made by dissolving thorium nitrate in water and was standardised both gravimetrically and volumetrically. The gravimetric standardisation involved the precipitation of thorium sebacate, followed by ignition to thoria at 1100°C[7], whereas the volumetric determination involved direct titration with ethylenediaminetetraacetic acid (EDTA) to the pyrocatechol violet end-point. Results by these two methods agreed to within 0.1%. Suitable aliquots of this solution were transferred to 100 ml beakers, followed by the requisite volumes of a solution of bismuth metal dissolved in nitric acid. The combined solutions were evaporated almost to dryness on the hot plate and the evaporation process was repeated twice in the presence of concentrated hydrochloric acid to remove most of the nitric acid from the sample. After solution of the residue in 50 ml of 10% v/v hydrochloric acid, the solution was allowed to flow through a column of Deacidite FF at a rate of 1.5 to 2 ml per minute. The level of the solution was allowed to fall to that of the top of the resin and then the column was washed five times with separate 10 ml portions of 10% v/v hydrochloric acid. The total eluant was collected in a 250 ml conical beaker and evaporated to very low volume. Then 2-5 ml of perchloric acid was added and the wet oxidation of organic matter carried out by the dropwise addition of concentrated nitric acid.

For the determination of milligram amounts of thorium, the solution after wet oxidation was diluted to a volume of about 50 ml with water. Then 2-3 drops of a 0.1% solution of pyrocatechol violet was added and the pH of the solution adjusted to a value in the range 3.0 to 3.2. Finally the thorium content was determined by direct titration with 0.02*M* EDTA solution. The complete removal of organic matter from solution is essential to obtain distinct colour changes of the indicator at the end-point. In cases when slightly masked end-points were produced, it was found useful to slightly over-titrate with EDTA and then back-titrate to the end-point with a standard 0.02*M* thorium nitrate solution. This titration procedure in the vicinity of the end-point could be repeated two or three times.

With amounts of thorium of 1 mg or less, the solution remaining after wet oxidation was evaporated to dryness and the residue dissolved in 1 ml of concentrated hydrochloric acid. This solution was transferred to a 100 ml graduated flask, 10 ml of a 0.1% thoronol solution was added and the final solution diluted to the mark with water. The thoronol reagent was prepared by dissolving 250 mg of the sodium salt of 1-(*o*-arsenophenylazo)-2-naphthol-3.6-disulphonic acid in water and diluting to 250 ml. Absorbancy measurements were taken with the Spekker absorptiometer fitted with Ilford 605 filters using a blank solution containing 1 ml of concentrated hydrochloric acid and 10 ml of 0.1% thoronol solution in 100 ml. Then the thorium content was determined by referring the reading to a previously prepared calibration graph. The size of absorptiometer cell depended on the thorium content, a 4 cm cell being used for the range 40 to 250 µg and a 1 cm cell for greater amounts up to 1200 µg.

Results on synthetic solutions covering the alloy compositions from 0.05% thorium up to approximately 10% are given in Table I. A complete blank determination carried out on the bismuth used in the preparation of the solutions, showed that no interference was caused in the determination of thorium. In sample analysis complete solution of the alloy is readily obtained in nitric acid and then the above procedure is directly applicable.

TABLE I

THE DETERMINATION OF THORIUM IN BINARY MIXTURES WITH BISMUTH

	Bi taken mg	*Th taken* mg	*Th in mixture* %	*Th found by analysis* mg	*Th by analysis* %
1	500	5.07	1.00	5.05[a]	1.00
2	500	25.50	4.86	25.50[a]	4.86
3	500	50.65	9.20	50.60[a]	9.19
4	100	0.047	0.047	0.048[b]	0.048
5	100	0.47	0.47	0.47[b]	0.47
6	100	1.05	1.04	1.04[b]	1.03

[a] volumetric determinations
[b] absorptiometric determinations

The separation and determination of uranium in the presence of bismuth

For the experimental work on this separation, a solution of uranium was prepared from U_3O_8 freshly ignited at 1100°C by dissolving a weighed amount in dilute nitric acid, evaporating the solution to low bulk and then diluting to volume with water in a suitable graduated flask. The final uranium content of this solution was checked volumetrically by the lead reductor method. This simply involved repeated evaporation of the solution to dryness in the presence of hydrochloric acid to remove nitric acid completely from solution, then passage of the hydrochloric acid solution through the lead reductor and finally titration of the tetravalent uranium with ceric sulphate using ferroin as the indicator. Aliquots of the uranium solution were combined with requisite volumes of a bismuth solution in nitric acid and then evaporated down with hydrochloric acid to remove most of the nitric acid from solution. The uranium was next separated from the bismuth by exactly the same procedure described previously for the bismuth-thorium mixtures. After wet oxidation of the eluant from the ion-exchange column with nitric and perchloric acids, the solution was evaporated to dryness and the evaporation process repeated in the presence of hydrochloric acid to ensure the complete removal of nitric acid from solution. The residue was dissolved in 25% v/v hydrochloric acid using 20 ml for 5 to 10 mg amounts of uranium and 10 ml for smaller amounts, and the resulting solution was passed through the lead reductor followed by five 2-3 ml washes of 10% v/v hydrochloric acid. To the reduced solution 0.1 ml of 0.001 *N* ferroin solution was added, followed by 10 drops of phosphoric acid, and the uranium was titrated with a standard ceric sulphate solution. The lead reductor was prepared in a 10 ml burette (internal diameter 8 mm) with a glass wool plug inserted to hold the lead column and initially filled with 10% v/v hydrochloric acid. A quantity of finely divided lead (40-60 mesh) was washed with 50% v/v hydrochloric acid, then 10% v/v hydrochloric acid and stirred to break up the caked material just before transference to the burette. The lead was allowed to settle under its own weight by falling through the dilute acid until it filled about 6 inches of the burette. Before use the reductor was washed with 10 ml of 25% v/v hydrochloric acid containing a small amount of ferric iron, followed by 20-25 ml of 10% v/v hydrochloric acid.

For the determination of microgram amounts of uranium, the residue after the wet oxidation treatment was evaporated in the presence of hydrochloric acid to remove nitrates and finally dissolved in 1 ml of 25% v/v hydrochloric acid. This solution was passed through a micro lead reductor, followed by four washes each of 1 ml of water. This reductor was made in the same way as the macro reductor, but using a tube 3-4 mm internal diameter, 10 cm in length and closed at the bottom by a screw clip acting on polyvinyl chloride tubing. Sufficient lead was taken to give a column about 2 inches in length. The total reduced solution was collected in a 25 ml graduated flask, about 10-15 ml of AnalaR acetone added, then 0.5 ml of 0.1% thoronol and the solution then thoroughly mixed. More acetone was added to dilute the solution to the graduation mark and then the total solution was transferred to a clean dry 4 cm Spekker cell. Absorbancy readings were taken with a Spekker absorptiometer fitted with Ilford 605 filters using water as the reference solution. This value was corrected for that obtained in a blank determination consisting of the passage of 1 ml of 25% v/v hydrochloric acid and four 1 ml water washes through the reductor, followed by the addition of the acetone and thoronol reagents. The uranium content was finally obtained by reference to a previously prepared calibration graph covering uranium concentrations up to about 50 μg of uranium per 25 ml of final solution.

The above procedures were tested by applying them to the determination of uranium in the presence of various amounts of bismuth up to a maximum of 1 g. Complete recoveries of uranium were obtained in all cases as shown in the results of Table II. Blank determinations carried out on the bismuth used in this work showed that the blank was less than 2 μg of uranium when 1 g of bismuth was taken for analysis. In the analysis of metallurgical samples, solution of the material was readily effected in nitric acid before the application of the above procedure.

TABLE II

THE DETERMINATION OF URANIUM IN BINARY MIXTURES WITH BISMUTH

	Bi taken mg	*U taken* mg	*U in mixture* %	*U found by analysis* mg	*U by analysis* %
1	100	9.99	9.08	9.92[a]	9.02
2	500	5.00	0.99	4.97[a]	0.98
3	500	0.50	0.10	0.51[a]	0.11
4	1000	1.18	0.118	1.15[b]	0.115
5	1000	0.10	0.01	0.098[b]	0.0098
6	1000	0.01	0.001	0.01[b]	0.001

[a] volumetric determination
[b] absorptiometric determination

DISCUSSION OF RESULTS AND CONCLUSIONS

Separations with the anion exchange resin Deacidite FF have proved exceedingly useful for the separation of macro amounts of bismuth from small amounts of thorium and uranium, without any significant losses of these latter constituents. This separation procedure therefore represents an improvement over other methods for the separation of bismuth, especially those involving the precipitation of bismuth as sulphide or oxyhalide. The use of ion-exchange resins, however, introduces fresh problems in the subsequent determination of the separated elements. The most serious of these is the frequent need for the removal of organic matter taken into solution from the resin, since the introduction of a wet oxidation step considerably extends the time needed for the analysis. In spite of this criticism, however, ion exchange procedures will undoubtedly help to simplify some of the difficult separation problems which the metallurgical chemist will encounter in the analysis of metallurgical alloy systems in the future.

SUMMARY

Procedures are described for the determination of uranium (0.001-10%) and thorium (0.05-10%) in binary mixtures with bismuth. A preliminary separation of the bismuth is effected by the passage of a hydrochloric acid solution of the sample through a column of Deacidite FF. For thorium contents greater than 1%, the determination is completed volumetrically with EDTA using pyrocatechol violet as indicator; smaller amounts are determined absorptiometrically with thoronol. Similarly the higher uranium contents are determined volumetrically after reduction to the tetravalent state with a lead reductor, and an absorptiometric method based on the coloured complex formed by tetravalent uranium with thoronol is used for the smaller amounts.

RÉSUMÉ

Des méthodes sont décrites pour le dosage de l'uranium (0.001 à 10%) et du thorium (0.05 à 10%) dans des mélanges binaires avec le bismuth. Une séparation préliminaire du bismuth est

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effectuée par passage d'une solution chlorhydrique de l'échantillon à travers une colonne de Deacidite FF. Pour des concentrations en thorium plus fortes que 1%, le dosage s'effectue volumétriquement au moyen d'EDTA, en utilisant le violet de pyrocatéchine comme indicateur; dans le cas de quantités plus faibles on effectue un dosage absorptiométrique avec le sel de sodium de l'acide 1-(*o*-arsénophényl-azo)-2-naphtol-3,6-disulfonique („thoronol"). De même des teneurs élevées en uranium peuvent être dosées volumétriquement après réduction à l'état tétravalent au moyen du réducteur au plomb; une méthode absorptiométrique basée sur la formation du complexe coloré formé entre l'uranium(IV) et le „thoronol" est proposée pour les quantités plus faibles.

ZUSAMMENFASSUNG

Verfahren für die Bestimmung von Uran (0.001-10%) und Thorium (0.05-10%) in binären Gemischen mit Wismuth werden beschrieben. Eine vorläufige Trennung des Wismuths wird erreicht indem man eine salzsaure Lösung der Probe durch eine Säule von Deacidite FF führt. Für Thoriumgehalte welche grösser sind als 1% wird die Bestimmung volumetrisch mit EDTA und Pyrocatecholviolett als Indikator beendet; kleinere Mengen werden absorptiometrisch mit Thoronol bestimmt. Auf ähnliche Weise werden die grösseren Urangehalte volumetrisch nach Reduktion in den vierwertigen Zustand mit einem Bleireduktor bestimmt, und wird eine absorptiometrische Methode, welche sich auf die gefärbte Komplexverbindung des vierwertigen Urans mit Thoronol gründet, für die kleineren Mengen verwendet.

REFERENCES

[1] K. A. Kraus and F. Nelson, *International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1955, Paper 837.

[2] M. Malat, V. Suk and O. Ryba, *Collection Czechoslov. Chem. Communs.*, 19 (1954) 679.

[3] P. F. Thomason, M. A. Perry and W. M. Byerly, *Anal. Chem.*, 21 (1949) 1239.

[4] A. Bacon and G. W. C. Milner, *Atomic Energy Research Establishment*, Report C/R 1813, H.M. Stationery Office, 1956.

[5] C. W. Sill and H. E. Peterson, *Anal. Chem.*, 24 (1952) 1175.

[6] J. K. Foreman, C. J. Riley and T. D. Smith, *XVth Congress of Analytical Chemistry of the International Union of Pure and Applied Chemistry*, Lisbon, 1956, Section VI, Paper 11; *Analyst*, 82 (1957) 89.

[7] I. Vogel, *Textbook of Quantitative Inorganic Analysis*, 2nd Edition, Longmans Green and Co., London, 1951.

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ÜBER DIE GENAUIGKEIT DER POLAROGRAPHISCHEN METHODE DER STANDARDZUGABE

von

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Die von H. Hohn[1] geschaffene Methode der Standardzugabe (des Eichzusatzes) hat, besonders in der von M. Spálenka[2] durchgeführten Abänderung, in der polarographischen Praxis breite Anwendung gefunden. Indem Hohn diese Methode vorschlägt, hebt er hervor, dass die Genauigkeit derselben ±3% ist, ohne die Bedingungen unter denen diese erzielt wird zu besprechen. L. Meites[3] der die Bedingungen unter welchen die genauesten Resultate erzielt werden, eingehend behandelt, behauptet, dass es zwecks Erreichen einer Genauigkeit von 2.5% notwendig sein würde, die Stufenhöhe nach erfolgter Standardzugabe mindestens zehn Mal grösser zu gestalten als diejenige der untersuchten.

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Über diese Betrachtungsweise müssen einige Bemerkungen gemacht werden:

1. Der Autor diskutiert nicht separat die Methode der Standardzugabe bei konstantem und bei veränderlichem Volumen. Wie weiter nachgewiesen wird, ist das Verhältnis der Stufenhöhen, bei denen maximale Genauigkeit erzielt wird, bei der einen und bei der anderen Variante verschieden.

2. Der Verfasser nimmt die relative Genauigkeit bei der Bestimmung der einzelnen Stufenhöhen als konstant an. Beim Aufnehmen der Polarogramme mit unveränderter Empfindlichkeit des Galvanometers[4] erscheint die absolute Genauigkeit – Δh konstant. Bei einem bedeutenden Wert des Verhältnisses der Grenzströme z.B. 1 : 10, wird aus diesem Grunde die relative Genauigkeit bei der Bestimmung der Höhe der niedrigeren Stufe stark verkleinert.

3. Beim Arbeiten in Anwesenheit adsorbierender Niederschläge nach Spálenka wird die relative Änderung der Konzentration der zu bestimmenden Komponente infolge Adsorption eine verschiedene sein, was gleichfalls den Fehler der Bestimmung vergrössern wird.

Obige Betrachtungen veranlassten uns, die Frage über die Genauigkeit der Methode der Standardzugabe von neuem zu erörtern.

1. Standardzugabe bei konstantem Volumen

In diesem Falle wird der Gehalt der zu bestimmenden Substanz in der untersuchten Probe nach folgender Formel bestimmt:

$$x = \frac{h}{H - h}\, a$$

x ist die zu bestimmende Komponente in g,
h die Stufenhöhe vor der Zugabe der Standardlösung,
H die Stufenhöhe nach Zugabe der Standardlösung,
a die Standardzugabe in g.

Unter der Voraussetzung, dass a mit genügend grosser Genauigkeit, z.B. mit einem Fehler von 0.2% bestimmt wird, wird der relative Fehler von x nach der Formel

$$\frac{\Delta x}{x} = \frac{\Delta h}{h} + \frac{\Delta H}{H - h} + \frac{\Delta h}{H - h}$$

ermittelt.

Beim Anwenden einer konstanten Empfindlichkeit des Galvanometers, sind die absoluten Fehler bei der Bestimmung der Stufenhöhen untereinander gleich ($\Delta h = \Delta H$). In diesem Falle gestaltet sich obige Formel folgendermassen:

$$\frac{\Delta x}{x} = \frac{\Delta H}{h} + \frac{\Delta H}{H - h} + \frac{\Delta H}{H - h}$$

Wenn $h = \lambda H$, wo $1 > \lambda > 0$ gesetzt wird, erhält man

$$\frac{\Delta x}{x} = \left(\frac{1}{\lambda} + \frac{2}{1 - \lambda}\right)\frac{\Delta H}{H}$$

Der Ausdruck $\frac{1}{\lambda} + \frac{2}{1-\lambda}$ hat sein Minimum bei $\lambda = 0.41$. Daraus folgt, dass das günstigste Verhältnis der Höhen $h : H = 1 : 2.5$ beträgt. Die Menge des Standardzusatzes muss also um 1.5 Mal grösser sein, als diejenige der zu bestimmenden Komponente. Obiges Ergebnis ist hinsichtlich der Genauigkeit dieser Methode keineswegs ermutigend, weil bei diesem Verhältnis der Stufenhöhen der relative Fehler bei der Bestimmung von x 6 Mal grösser ist, als derjenige von H.

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2. *Methode der Standardzugabe bei veränderlichem Volumen*

In diesem Falle wird der Gehalt des zu bestimmenden Stoffes nach der Formel

$$x = \frac{h\,V_2\,C}{H\,(V_1 + V_2) - h\,V_1}$$

ermittelt. Dabei ist C der Titer der Standardzugabe, V_1 das Volumen der untersuchten Lösung und V_2 das Volumen des Standardzusatzes.

Ausser den bereits gemachten Voraussetzungen und Substituierungen setzen wir bei dieser Betrachtung $V_2 = \beta V_1$, wo β positiv ist, ein. Dadurch erhält man

$$\frac{\Delta x}{x} = \left(\frac{1}{\lambda} + \frac{2+\beta}{1+\beta-\lambda}\right)\frac{\Delta H}{H}$$

Für das Minimum des Ausdruckes $\dfrac{1}{\lambda} + \dfrac{2+\beta}{1+\beta-\lambda}$ erhält man $\lambda = -1 + \sqrt{2+\beta}$.

Bei $\beta = 2$* wird $\lambda = 1$. Bei diesen Werten wird der relative Fehler von x drei Mal grösser als derjenige von H sein. Ferner folgt aus obigem Ausdruck, dass bei konstantem λ (z.B. $\lambda = 1$) die Genauigkeit der Bestimmung mit Anwachsen von β zunimmt.

Die angeführten Schlussfolgerungen bestätigen die Annahme, dass bei der Methode der Standardzugabe bei veränderlichem Volumen, eine maximale Genauigkeit erreicht wird, wenn die Konzentration der Standardlösung nahe derjenigen der untersuchten Lösung liegt, während das Volumen der Standardlösung im Vergleich zum Volumen der untersuchten Lösung möglichst gross ist.

Es muss ferner betont werden, dass diese Schlussfolgerung bei der Bestimmung von Depolarisatoren, bei welchen die Gleichung von Ilkovič nicht gilt, gute Möglichkeiten in Aussicht stellt. Wegen der geringen Konzentrationsunterschiede beider Lösungen nehmen die Fehler, die auf die Unproportionalität zwischen Stufenhöhe und Konzentration des Depolarisators zurückzuführen sind, ab. Bei vollkommen gleichen Konzentrationen werden sie eliminiert.

Auf Grund der Ergebnisse dieser Diskussion lässt sich eine Änderung der Eichzusatzmethode bei konstantem Volumen bezw. eine Umwandlung derselben in eine Methode mit veränderlichem Volumen gestalten. Um die Genauigkeit der Methode von Spálenka zu erhöhen, schlagen wir folgende Arbeitsweise vor:

In 2 Kolben verschiedenen Volumens, z.B. von 25 und von 100 ml, wird das gleiche Volumen der untersuchten Lösung gesetzt. In dem Kolben mit dem grösseren Volumen wird soviel Standardlösung zugegeben, dass nach erfolgtem Nachfüllen bis zur Marke, die Konzentration des Depolarisators darin nahe derjenigen in dem kleinen Kolben liegt. In dem behandelten Beispiel mit Kolben von 25 und 100 ml muss die Menge der Standardzugabe dreimal grösser sein als diejenige, welche in der untersuchten Lösung enthalten ist. Beide Lösungen werden auf dieselbe Weise behandelt und danach bis zur Marke gefüllt. Bei dieser Modifikation der Methode sind die Konzentrationen der zu bestimmenden Komponente in den beiden Proben sehr nahe; infolgedessen vermindern sich die Fehler, die von der Adsorption und von der unproportionellen Abhängigkeit zwischen dem Grenzstrom und der Konzentration des Depolarisators verursacht sind. Die Berechnung der gesuchten Konzentration wird nach der Formel für die Standardzugabe bei veränderlichem Volumen durchgeführt. In Einklang mit den gemachten Betrachtungen, hängt der relative Fehler von dem Verhältnis der Volumina ab. Bei dem angeführten Beispiel beträgt er 2.7%.

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* Bei grösseren Werten von β geht λ über den Definitionsintervall $0 < \lambda < 1$ hinaus. Die Betrachtungen bei solchen Werten verlieren folglich ihren physikalischen Sinn.

SCHLUSSFOLGERUNGEN

Es wurde festgestellt:

1. Dass bei der Methode der Standardzugabe bei konstantem Volumen der minimale Fehler bei einem Verhältnis der Stufenhöhen von 1 : 2.5 erzielt wird.

2. Dass bei der Methode der Standardzugabe bei veränderlichem Volumen der minimale Fehler bei einem Verhältnis der Stufenhöhen von 1 : 1 und bei möglichst grossem, gegenüber dem Volumen der untersuchten Lösung, Volumen der Standardzugabe, erreicht wird.

Um die Genauigkeit der Methode von Spálenka zu erhöhen, wird eine neue Modifikation vorgeschlagen, bei der diese Methode in eine Methode bei veränderlichem Volumen umgewandelt wird.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit sind die Bedingungen behandelt worden, unter welchen die relative Genauigkeit der Methode der Standardzugabe maximal ist, dabei von dem Umstand ausgehend, dass bei einer Bestimmung der absolute Fehler beim Abmessen der Höhen der einzelnen Stufen konstant ist. Beide Varianten der Methode — diejenigen bei konstantem und bei veränderlichem Volumen — wurden diskutiert. Im ersten Falle wird eine maximale Genauigkeit bei dem Verhältnis der Stufenhöhen 1 : 2.5 erreicht. Im zweiten Falle wird dies bei dem Verhältnis 1 : 1 und unter Anwendung eines möglichst grossen Volumens der Standardzugabe verwirklicht. Da die Genauigkeit, welche erzielt werden kann, bei der Methode mit veränderlichem Volumen höher ist, wird eine Modifikation der Methode von M. Spálenka vorgeschlagen.

SUMMARY

In this article the conditions have been considered under which the relative precision of the standard addition method is maximum, keeping in mind that for a determination, the absolute error in determining the heights of the separate waves is constant. Both variants of the method have been considered: by constant volume and by changeable volume. In the first case, the maximum precision is attained for a ratio 1 : 2.5 of the heights of the waves; in the second case, for a ratio 1 : 1 and greatest possible volume of the standard addition.

As attainable precision is greater in the method with changeable volume, a variation of M. Spálenka's method is proposed.

RÉSUMÉ

Dans cet article sont considerées les conditions dans lesquelles la précision relative de la méthode de l'addition standard atteint au maximum en tenant compte du fait que, pour une détermination, l'erreur absolue de la mesure des hauteurs des vagues est une valeur constante. Sont considerées les deux variantes de cette méthode: lorsque le volume est constant et lorsqu'il est variable. Dans le premier cas on atteint à la précision maximum lorsque le rapport des hauteurs des vagues est 1 : 2.5; dans le deuxième cas pour un rapport 1 : 1 et le plus grand volume possible de l'addition standard. Comme la précision à laquelle on peut atteindre est plus grande quand on a recours à la méthode du volume variable, une modification de la méthode de M. Spálenka est proposée.

LITERATUR

[1] H. Hohn, *Chemische Analysen mit dem Polarographen*, Springer Verlag, Berlin, 1937.

[2] M. Spálenka, *Polarografické methody v metalurgii*, Statni nakladatelstvi technické literatury, Praha, 1954.

[3] L. Meites, *Anal. Chem.*, 28 (1956) 139.

[4] J. Kůta und As. Trifonow, *Einführung in die Polarographie* (bulg.), Nauka i iskustwo, Sofia, 1955.

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MICRO-HETEROMETRIC DETERMINATION OF CADMIUM WITH SODIUM DIETHYLDITHIOCARBAMATE

by

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INTRODUCTION

The heterometric determination of cadmium with sodium diethyldithiocarbamate (= CBM) can be made either in acetate solution or, more successfully, in ammoniacal citrate solution. The molar sensitivity of the reaction is high ($\sim 0.00025 M$) and of the same order of magnitude as with copper and zinc carbamates. Approximately 0.5 mg cadmium in 20 ml solution can be determined, under appropriate conditions, in 10-15 minutes. The solutions may contain 99-99.9% of the following foreign metals as cations: Mg^{+2}, Ca^{+2}, Ba^{+2}, Zn^{+2}, Mn^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, Sb^{+3} and Pb^{+2}. Except in special cases the error was less than 1%. The sensitivity of the reaction remains the same whether the determination is made in the presence or absence of foreign metals.

EXPERIMENTAL

The working conditions were the same as in the determination of zinc with carbamate*. The literature on heterometry is given there.

RESULTS AND DISCUSSIONS

Table I and Fig. 1 present a selection of experiments made and the results obtained. In the titrations of cadmium with CBM the following difficulty was encountered: during the titration, almost immediately after the first maximum density point was reached, the density dropped causing fluctuations in the density values and thus the fixation of the end-point of the titration was difficult. This was probably caused by the influence of free CBM on the physical state of the insoluble carbamate presumably causing coagulation. It was found that the addition of a small quantity of ethyl alcohol stabilised the horizontal maximum density line. Too much alcohol dissolved the precipitate partly, the initial precipitation occurring late and the maximum density value being rather low (exp. 5). In the presence of large amounts of ammonia, either with or without complexing agents such as tartrate or citrate, the horizontal maximum density line was also stabilised (exps. 4, 8 and 9).

Experiments in the absence of foreign metals

In acetic acid (pH ~ 3) or in acetate-acetic acid (pH ~ 4.7) solution (exps. 1 and 2) the maximum density value is lower than in neutral or acetate solution (exp. 3). In

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* M. BOBTELSKY AND R. RAFAILOFF, *Anal. Chim. Acta*, 15 (1956) 457 (See literature on heterometry).

TABLE I

Composition: 5 ml 0.001 M $Cd(NO_3)_2$ + a ml supplements + (15 — a) ml H_2O + x ml 0.0025 M sodium diethyldithiocarbamate (=CBM). T = 20°C. Content: 0.5621 mg Cd. Concentration: 0.00025 M.

Expt. no.	*Supplements*	*% Cd*	*found*				
			ml CBM (x)	*Maximum density value*	*Initial precip. at ml*	*Titration time (min)*	*% error*
1	2 ml M CH_3COOH		4.03	0.26	0.6	12	0.7
2	1 ml M CH_3COOH + 1 ml M CH_3COONa		3.96	0.34	0.4	13	1.0
3	15 ml H_2O		4.06	0.57*	0.4	15	1.5
4	1 ml conc. NH_4OH + 1 ml 2M NH_4NO_3		3.96	0.65	0.0	11	1.0
5	0.5 ml conc. NH_4OH + 2 ml 2M NH_4NO_3 + 10 ml alcohol		4.00	0.40	1.2	21	3.0
6	8 ml 0.125M $Na_4P_2O_7$		4.00	0.43*	0.6	20	0.0
7	8 ml 0.25M $Na_5P_3O_{10}$		4.00	0.53	0.2	18	0.0
8	6 ml M K_2-tartrate + 1 ml conc. NH_4OH + 5 ml alcohol		4.00	0.57	0.4	12	0.0
9	6 ml M Na_3-citrate + 1 ml conc. NH_4OH + 5 ml alcohol		4.00	0.54	0.2	13	0.0
10	1 ml M CH_3COONa + 5 ml M $Mg(NO_3)_2$	0.5	4.00	0.53+	0.6	15	0.0
11	5 ml M $Mg(NO_3)_2$ + 3 ml M Na_3-citrate + 0.5 ml conc. NH_4OH		4.02	0.58	0.2	8	0.5
12	5 ml M $Mg(NO_3)_2$ + 4 ml 2M NH_4NO_3 + 0.5 ml conc. NH_4OH + 5 ml alc.		4.00	0.55	0.2	13	0.0
13	5 ml M $Ca(NO_3)_2$ + 3 ml M Na_3-citrate + 0.5 ml conc. NH_4OH		3.95	0.38*	0.4	9	1.2
14	5 ml 2M $Ca(NO_3)_2$ + 2 ml 2M NH_4NO_3 + 0.5 ml conc. NH_4OH + 5 ml alc.	0.2	4.00	0.58	0.4	10	0.0
15	5 ml 2M $BaCl_2$ + 2 ml 2M NH_4NO_3 + 0.5 ml conc. NH_4OH + 2.5 ml alc.	0.04	4.00	0.59	0.4	8	0.0
16	4 ml 2M $Zn(NO_3)_2$ + 10 ml M Na_3-citrate + 1 ml conc. NH_4OH	0.1	4.00	0.55	0.4	10	0.0
17	2 ml M $MnCl_2$ + 3 ml M Na_3-citrate + 1 ml conc. NH_4OH	0.5	4.03	0.55	0.4	13	0.7
18	3 ml M $Al(NO_3)_3$ + 6 ml M Na_3-citrate + 1 ml conc. NH_4OH	0.7	3.90	0.50	0.6	12	2.5
19	1 ml M $Cr(NO_3)_3$ + 3 ml 2M CH_3COONa	1.0	3.90	0.41	0.4	7	2.5
20	3 ml M $Fe(NO_3)_3$ + 10 ml M Na_3-citrate + 1 ml conc. NH_4OH	0.3	4.00	0.45	0.6	6	0.0
21	5 ml 0.4M $SbCl_3$ (+ 2M HCl) + 6 ml M K_2-tartrate + 1.5 ml conc. NH_4OH	0.2	3.92	0.31	0.6	12	2.0
22	3 ml M $Pb(NO_3)_2$ + 10 ml M Na_3-citrate + 1 ml conc. NH_4OH	0.10	4.00	0.45	0.2	10	0.0

* short horizontal line; + after the maximum sudden drop

addition no horizontal maximum density line was obtained. In ammoniacal ammonium nitrate solution (exps. 4 and 5) the reaction was smooth. Probably pyro- and tripolyphosphate could also be used as complexing agents (exps. 6 and 7). Large amounts of alkali citrate or tartrate had no influence when used in solutions containing large amounts of ammonia (exps. 8 and 9). In both the latter cases a horizontal maximum line was obtained immediately after the first maximum density point. Cadmium did not precipitate in the presence of disodium ethylenediaminetetraacetate (= Na_2EDTA) (0.1*M*) either in acetate or in ammoniacal solution. In acetic acid solution the maximum density value was low and the end-point was uncertain.

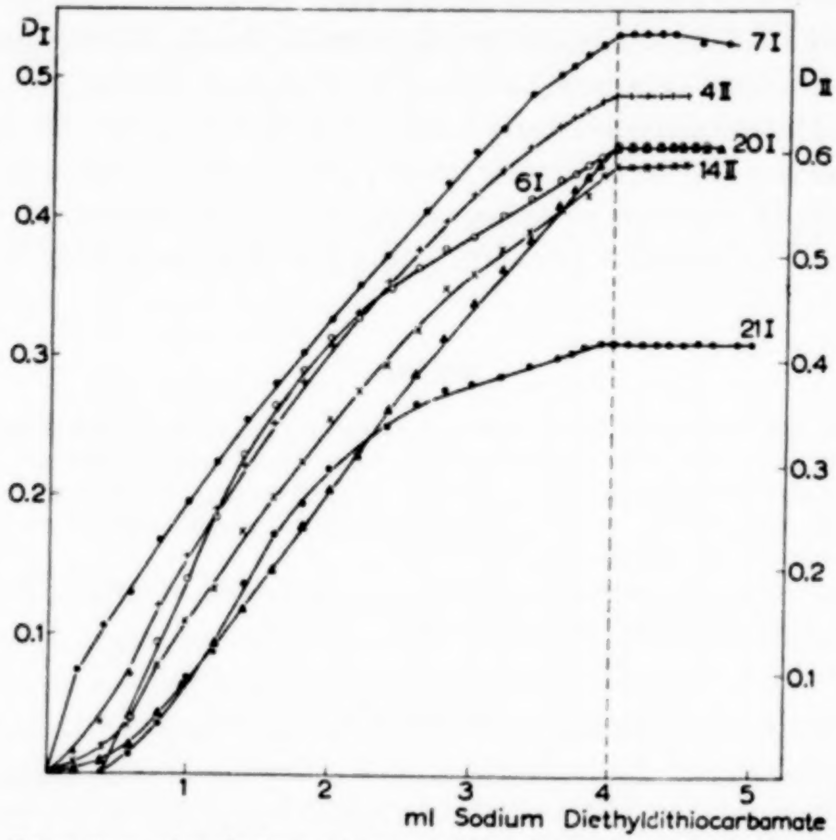

Fig. 1. Titrations of cadmium nitrate with sodium diethyldithiocarbamate.

Experiments in the presence of foreign metals

Large amounts of trisodium citrate were most successfully used for complexing the foreign bi- or trivalent cations in ammoniacal solution. The horizontal maximum density line was stable. The table only gives the final composition of the experiments, showing the most successful experiment and the most favourable conditions. In almost all cases presented, the foreign metal made up 99% or more of the total metal content in the analysed solution.

It may be seen that the cadmium made up only 0.1% in the solutions of *calcium*, *barium* and *magnesium* (exps. 12, 14 and 15). Even in the *zinc nitrate* solution which contained very large amounts of Na_3-citrate, the cadmium made up no more than 0.1% and the latter could be determined with an error close to zero (exp. 16). The amount of *manganese* in exp. 17 is probably the maximum which can be present in the cadmium solution. No suitable complexing agent could be found for *nickel* or *cobalt* even when present in low concentrations (0.05*M*). At this concentration in the citrate solution the maximum density value obtained was low and no end-point could be reached.

No method was found for the direct determination of cadmium in solution containing *copper* or *mercuric* salts, even if the latter were in very low concentration. As exp. 22 shows, *lead* which made up 99.9% of the total, could be complexed successfully with ammoniacal citrate, and the error was close to zero. As to the trivalent cations, because of the insolubility of the *chromium* citrate, acetate was used instead as complexing agent (exp. 19). In *ferric iron* solution (99.7% iron) the amount of citrate used was extremely large. The maximum density value seemed to be somewhat lower than usual but the error was close to zero. Similar good results were obtained in *aluminium* salt solution (exp. 18). In the case of *antimony* (99.8%) only potassium tartrate could be used successfully. The maximum density value was depressed (exp. 21).

METHOD

20 ml of aqueous solution containing about 0.5 mg of cadmium, in addition to 3-10 ml of M Na_3-citrate + 1 ml conc. NH_4OH, are titrated at room temperature with a ∼ 0.0025M sodium diethyldithiocarbamate. The solution may contain 99% to 99.9% of calcium, barium, magnesium, zinc, manganese(II), aluminium, chromium(III), iron(III), antimony(III) or lead. The titration time is 10-15 minutes and the error is generally 0-1%.

Remark: In the presence of antimony, tartrate is used instead of citrate. When no foreign salt is present, ammonium nitrate may be used instead of citrate.

SUMMARY

0.5 mg of cadmium in 20 ml aqueous solution can be determined heterometrically at 20°C with sodium diethyldithiocarbamate. The solution may contain 99-99.9% of Ca, Ba, Mg, Zn, Mn, Al, Cr(III), Fe(III), Sb(III) or Pb. Titration time: 10-15 min. Error generally 0-1%.

RÉSUMÉ

Le cadmium (0.5 mg/20 ml) peut être dosé, en solution aqueuse, par la méthode hétérométrique, au moyen du diéthyldithiocarbamate de sodium. La solution peut contenir 99-99.9% de Ca, Ba, Mg, Zn, Mn, Al, Cr(III), Fe(III), Sb(III) et Pb. Le temps nécessaire au dosage est de 10-15 min. Erreur: 0-1%.

ZUSAMMENFASSUNG

0.5 mg Cadmium kann heterometrisch bei 20°C in 20 ml wässriger Lösung mit Hilfe von Natriumdiäthyldithiokarbamat bestimmt werden. Die Lösung kann 99-99.9% von Ca, Ba, Mg, Zn, Mn, Al, Cr(III), Fe(III), Sb(III) und Pb, enthalten. Titrationszeit: 10-15 Min. Fehler: 0-1%.

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THE PREPARATION OF SAMPLES FOR α-COUNTING BY THE DIRECT EVAPORATION OF ORGANIC SOLUTIONS

by

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INTRODUCTION

Many of the difficulties which arise in the radiometric analysis of solutions of α-emitting nuclides in organic solvents are due to certain physical properties peculiar to these solvents. In particular, it is impossible to evaporate such a solution onto the flat stainless steel or platinum discs normally used for α-counting, because of the low surface tension of such solutions. Back-extraction of the element in question into an aqueous phase is, of course, generally possible but is often either inconvenient or undesirable. A number of previous attempts have been made in this department to find methods of maintaining the solution in position during evaporation. A technique based on the use of an absorbent pellet or mound of ammonium carbonate has been used, but this is slow in operation and mechanical loss of solid can easily occur during heating.

The method described below has been developed in connection with work on the ion exchange behaviour of α-emitting elements in organic solvents[1]. This overcomes the problem by applying a temperature gradient from the edge of the tray to the centre by heating the periphery on a metal cylinder. The solution is prevented from overrunning the edge of the tray and evaporates smoothly to give a deposit which has been shown to be eminently suitable for α-counting. The technique of periphery heating for aqueous solutions has been described by KOHMAN, AMES AND SEDLET[2], and in rather more elaborate detail by WESTRUM[3]. Details of the method are given, with the results of testing on a semi-routine basis.

EXPERIMENTAL

Apparatus

Stainless steel counting trays, 1 inch diameter and highly polished on one side only were used. Early experiments were carried out with a copper heating block (Fig. 1A; the diagram in fact shows the final result of a series of semi-arbitrary modifications to an originally thicker copper cylinder). The source of heat was either an electrical hot plate, or preferably, an inverted infrared heater; in later developments, electrically heated aluminium cylinders (Fig. 1B) have been used. For any solution, it is clear that the same conditions must apply; the heat input is balanced by radiation, conduction and convection losses from the cylinder, plus the heat necessary to evaporate the solvent. Significant alteration of any one of these factors necessitates a re-adjustment of the rate of heating necessary for smooth evaporation. We have not found it necessary to cool the centre of the tray with a current of air.

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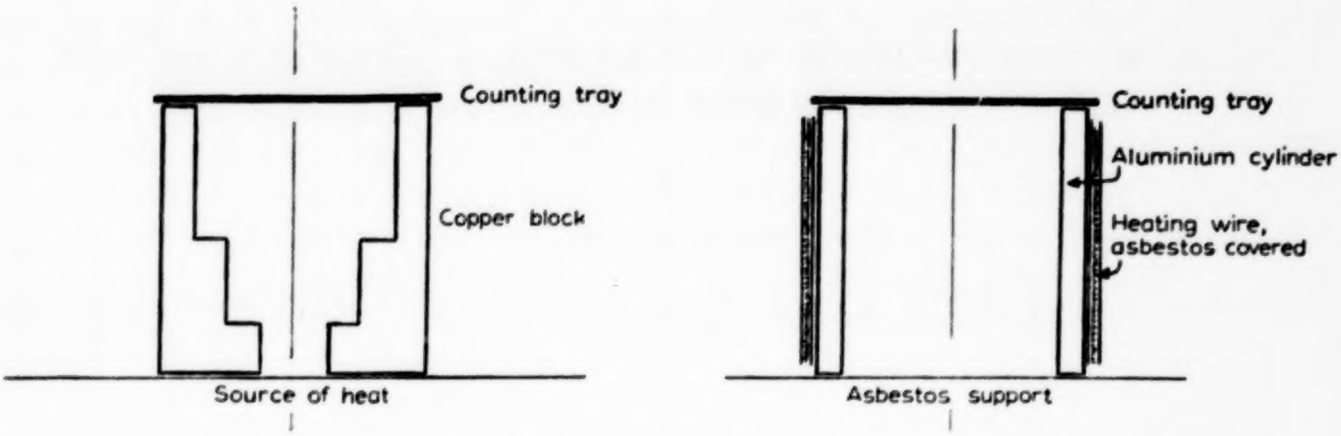

Fig. 1. Apparatus for periphery heating of counting trays.
1A. Original method. 1B. Electrically heated aluminium cylinder.

Procedure

The surface of the tray must be perfectly horizontal and this is best tested by examining the movement of a comparatively large drop of pure solvent, both at room temperature and under working conditions. With the heater raised to the requisite temperature (see below) a suitable aliquot is withdrawn with a micro-pipette from the solution under investigation. The counting tray is then carefully placed on the heating block and the aliquot of solution immediately pipetted onto the centre of the tray. The tray should have been cleaned and degreased by an acetone wash, and should have a bright unoxidised surface to prevent the liquid spreading; to prevent oxidation, trays must not be left on the heater for an appreciable length of time before pipetting on the solution. For large aliquots it is advisable to add the solution dropwise, but amounts up to 50 μl can be kept in position quite easily, provided the tray is perfectly horizontal. We have examined three solvents — benzene, dibutylcarbitol, and tri-*n*-butyl phosphate in odourless kerosene (TBP/OK), and for each of these evaporation is complete in a few minutes. With the latter two solvents, provided that only invisible quantities of solute are present, the surface of the tray appears unchanged apart from a slight etch mark, the intensity of which apparently depends on the concentration of acid in the solution. The trays are finally heated to a dull red heat in a Meker burner before counting. For solutions of trifluorothiophenonylacetone in benzene, a slight deposit remains after evaporation but this is removed during the final heating of the tray.

Care must be taken with dibutylcarbitol solutions containing appreciable quantities of nitric or perchloric acids, since overheating initiates rapid decomposition of the solvent, with violent frothing and evolution of nitrous (or chlorous) fumes. This can be avoided by starting with the heater at a low temperature (*e.g.* $\sim$75°C). The aliquot, but not the washings, is pipetted onto the tray, which is then allowed to warm up. In this way, solvent decomposition can be avoided; should any reaction commence, as evidenced by the formation of small bubbles of gas, a drop of cold solvent will quench the decomposition effectively. The pipette washings are added as the volume of liquid on the tray becomes sufficiently reduced.

The periphery of the tray must obviously be hot enough to maintain the solution in position and at the same time the centre of the tray must not be so hot as to cause spitting (and hence mechanical loss of solution). Within these limits, the temperature of the heater does not appear to be very critical and is largely determined by the rate of evaporation desired and the properties of the solvent being used.

RESULTS AND DISCUSSION

Initial examinations of the possibility of using this technique were carried out with a solution of plutonium in dibutylcarbitol. Ten samples (50 μl aliquot) prepared in an hour gave a precision on any individual result of 11% (3σ). No loss of activity occurred during the final intense heating of the counting trays; in fact, slight increases were observed, presumably due to removal of moisture, dust, etc., from the surface of the deposit during heating. It was also shown that in a solution prepared by solvent extraction, the plutonium concentration found by this method corresponded almost exactly to the value calculated from the initial and final plutonium concentration in the aqueous phase.

A more thorough examination has been made for solutions of plutonium in TBP/OK. Twelve operators, with no previous experience of the technique, each carried out duplicate analyses on such a solution; the mean result had an overall precision of 15.7%. Examination of the pairs of results produced by individual operators suggests that some of this deviation may arise from pipetting errors. Back extraction of plutonium from this solution with an aqueous solution of ammonium carbonate revealed a negative bias of 8%. One possible explanation for this is that the complex formed by plutonium nitrate and tri-butyl phosphate[4] may be slightly volatile under the conditions of evaporation.

From the nature of the method of evaporation it is clear that the active material will be deposited within the heated periphery of the counting tray. This is confirmed by the etch marks on the surface, and by autoradiographic examination of the distribution of the activity. Two trays, carrying plutonium evaporated from dibutylcarbitol were left in contact with Ilford 'Nuclear Plate' for two days; the autoradiographs (Fig. 2) show that the deposit is quite well defined. There is some slight non-uniformity of distribution, presumably due to the shape of the temperature gradient across the tray. It is interesting that the autoradiographs demonstrate the complete absence of crystallite formation during evaporation. Alpha-pulse analysis of these sources showed that good definition could be achieved for the 5.15 Mev peak of plutonium-239; a resolution of 50 kev was found. The technique should, therefore, be applicable to the routine preparation of samples for kick-sorting. It has the advantage that the amount of activity deposited on the tray can be predicted exactly, which is not so for methods such as vacuum sublimation.

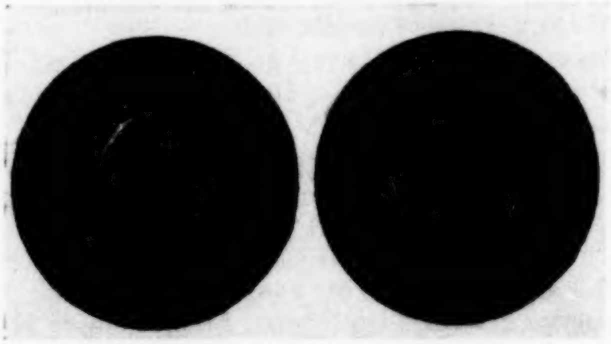

Fig. 2. Autoradiographs of plutonium deposited on stainless steel by evaporation of dibutylcarbitol solutions.

The technique described is superior in many respects, such as speed and ease of operation, to methods previously used (see Introduction). An additional advantage is that mechanical losses are reduced to a minimum and any errors due to spillage or losses from spitting during evaporation are immediately obvious to the operator.

ACKNOWLEDGEMENTS

I wish to thank Mrs. J. Y. FARDON for experimental assistance. The electrically heated aluminium cylinder was designed by Mr. B. ASTRIDGE. This work is published by permission of the Managing Director, Industrial Group, United Kingdom Atomic Energy Authority.

SUMMARY

A method is described for the preparation of thin deposits of α-emitting elements by evaporation of solutions in organic solvents. By heating the periphery of the tray, a suitable temperature gradient is maintained across the tray, giving smooth evaporation of the solvent to leave a deposit which is suitable for α-counting. It has been shown that on a semi-routine basis, the method is rapid and gives good precision.

RÉSUMÉ

Une méthode est décrite pour la préparation de dépôts minces d'émetteurs α par évaporation des solutions en solvants organiques. Par chauffage de la périphérie de la plaque, une pente de température convenable est maintenue, permettant une évaporation douce du solvant et l'obtention d'un dépôt convenable pour la mesure des particules α. La méthode est rapide et présente une bonne précision.

ZUSAMMENFASSUNG

Eine Methode zur Herstellung von dünnen Lagen von α-emittierenden Elementen durch Verdampfung von Lösungen in organischen Lösungsmitteln wird beschrieben. Durch Erhitzen der Peripherie der Platte wird ein geeigneter Temperaturgradient auf der ganzen Platte in Stand gehalten, welcher eine gleichmässige Verdampfung des Lösungsmittels ergibt, und einen Rückstand hinterlässt der zur α-Zählung geeignet ist. Bei halbroutine Bestimmungen gibt die Methode rasch genaue Ergebnisse.

REFERENCES

[1] D. G. Tuck and G. A. Welch, (to be published).

[2] T. P. Kohman, D. P. Ames and J. Sedlet, *The Trans-Uranium Elements*, National Nuclear Energy Series IV-14B, McGraw-Hill Book Co. Inc., New York, 1949. Paper 22.60, p. 1675.

[3] E. F. Westrum Jr., *ibid.*, Paper 16.2, p. 1185.

[4] T. V. Healy and H. A. C. McKay, *Trans. Faraday Soc.*, 51 (1956) 633.

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THE THERMAL DECOMPOSITION OF THE 2-METHYL-8-QUINOLINOL (8-HYDROXYQUINALDINE) CHELATES OF SCANDIUM, THORIUM, URANIUM (VI) AND THE RARE EARTH ELEMENTS

by

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The use of 8-quinolinol in analytical chemistry is well known. In an attempt to find a more selective chelating agent, numerous substituted quinolinols have been prepared. One of the interesting results of this search has been the introduction of the 2-methyl derivative, 2-methyl-8-quinolinol (8-hydroxyquinaldine, 2-methyl-oxine), as a chelating agent by Merritt and Walker[1]. It was found that this reagent would precipitate the same metal ions as 8-quinolinol except aluminum. Merritt and Walker[1] attributed this inability to precipitate aluminum as due to the increased size of the reagent molecule. Later, it was shown by Irving, Butler and Ring[2] that the methyl group in the 2-position exhibited a steric hindrance effect, thus preventing the formation of the aluminum chelate. This has been confirmed by potentiometric studies[3,4].

To determine if other trivalent metal ions would be precipitated, Phillips, Emery and Price[5] studied the reaction between yttrium, lanthanum, gallium, indium and scandium with 2-methyl-8-quinolinol. They showed that indium and scandium could be quantitatively precipitated, while yttrium and gallium appeared to be only partially precipitated. As with 8-quinolinol[6], the scandium chelate contained a molecule of solvation which could not be removed by drying at 105°C. The uranium chelate was also shown to contain an extra solvate molecule, while thorium, in contrast to the 8-quinolinol chelate, precipitated as the normal chelate.

The thermal decomposition of the Mg, Cu, Zn, Ni, Co, Tl, V and Mo chelates of 2-methyl-8-quinolinol has been studied on the thermobalance[7,8]. In general, it was found that the chelates were less stable thermally than those of 8-quinolinol[9] or of 2-phenyl-8-quinolinol[10]. The order of increasing stability for the anhydrous chelates was $\mathrm{Tl} < \mathrm{Cu} < \mathrm{V} < \mathrm{Zn} < \mathrm{Mo} < \mathrm{Co} < \mathrm{Ni} < \mathrm{Mg}$.

Previous thermobalance studies have shown that the solvate molecule in the 8-quinolinol chelates of uranium(VI) and thorium could be removed by heating, while the scandium chelate behaved differently in that the chelate decomposed instead of losing the extra solvate molecule[6]. Since 2-methyl-8-quinolinol forms the same types of chelates with these elements (except thorium) it was of interest to subject them to thermal decomposition on the thermobalance. Since little is known about the decomposition of other trivalent metal chelates, the rare earth metal chelates were also studied.

EXPERIMENTAL

Reagents. 2-Methyl-8-quinolinol was obtained from the Aldrich Chemical Company, Inc., Milwaukee 12, Wisc. It was used without further purification.

Scandium oxide of 99.8% purity was obtained from A. D. Mackay, Inc., New York 38, N. Y.; thorium nitrate tetrahydrate was obtained from the Lindsay Chemical Co., West Chicago, Ill.; uranium(VI) nitrate hexahydrate was obtained from Merck and Co., Inc., Rahway, N. J.; and the rare earth compounds were obtained as the oxides of 99.9% purity from the Lindsay Chemical Co., West Chicago, Ill., and Research Chemicals, Inc., Burbank, Calif.

All other reagents were of analytical reagent grade quality.

Thermobalance. The thermobalance used has been previously described[11]. The weight of the samples ranged from 90-100 mg. The heating rates on all samples were 4.5°/min with a maximum temperature limit of about 900°C. The weight of the sample was recorded to ± 0.1 mg, while the temperature was recorded to ± 1°C. Duplicate samples were run on each sample with a resulting agreement to each other within 1%.

Preparation of chelates. The scandium, thorium and uranium chelates were prepared as previously described[5].

The general procedure for the preparation of the rare earth chelates consisted of adding 0.2 to 0.3 g of the hydrated chloride or nitrate metal salt to 150 ml of water. A slight excess (10 to 20%) of 2-methyl-8-quinolinol solution 4% (w/v) in $2N$ acetic acid was added and the solution warmed to 60°C. To this solution, 10 ml of $2M$ ammonium acetate solution and a sufficient amount of $2N$ ammonium hydroxide solution were added to bring the final pH value to about 8.5. The precipitated chelates were allowed to stand at room temperature for two hours, filtered through sintered porcelain crucibles, washed twice with water, and allowed to air dry at room temperature for at least 24 hours.

DISCUSSION

2-Methyl-8-quinolinol. Thermal decomposition of the reagent was first studied to determine the temperature at which it can be sublimated from precipitated chelates. Merritt and Walker[1] stated that the co-precipitated reagent was volatile at 130°C, and thus recommended drying the zinc and magnesium chelates at 130 to 140°C. From the thermal decomposition curve as shown in Fig. 1, it can be seen that the reagent began to sublime at 90°C (atmospheric pressure about 680 mm Hg). At about 200°C, the reagent had completely sublimed, without decomposition, leaving the thermobalance pan empty. The behavior of this compound was very simliar to 8-quinolinol, which under these same conditions, began to sublime at 85°C[6]. From these results, it does not seem necessary to restrict the drying temperatures to 130 to 140°C.

Uranium. The thermal decomposition of the uranium 2-methyl-8-quinolinol chelate is shown in Fig. 1. As normally precipitated from solution, the chelate corresponded to the formula, $UO_2(C_{10}H_8NO)_2{\cdot}C_{10}H_8NOH$, similar to that of the 8-quinolinol chelate[6]. The solvated chelate was stable up to 55°C where it began to lose 2-methyl-8-quinolinol. A break in the curve was found at 258° which corresponded closely to the normal chelate, $UO_2(C_{10}H_8NO)_2$. The normal chelate was stable up to 290°C where it began to decompose to give U_3O_8, beginning at 480°C.

The stability range of the normal uranium 2-methyl-8-quinolinol chelate was much smaller than that of the 8-quinolinol chelate. In the case of the latter, it was stable from about 280 to 380°C, while in this case, it was 258 to 290°C.

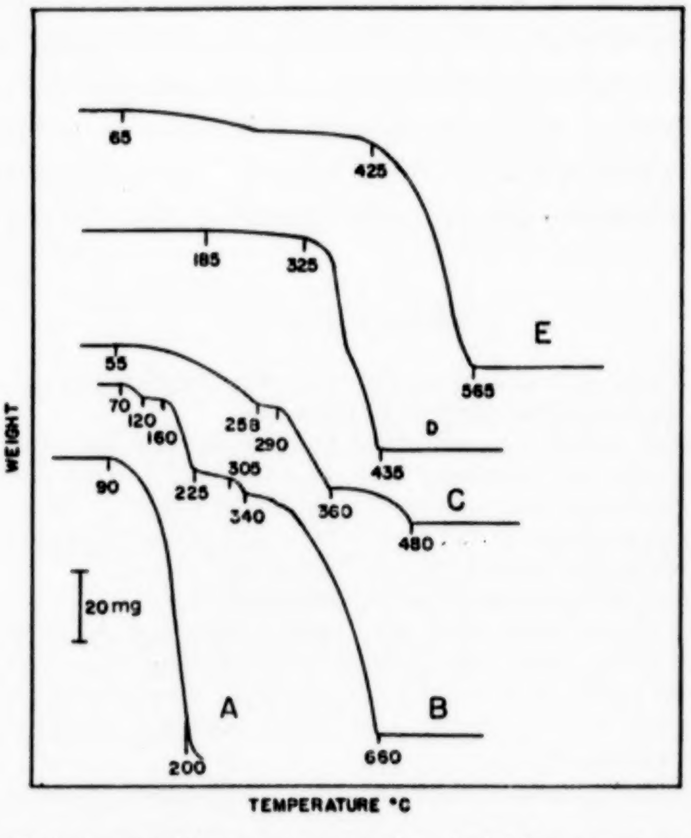

Fig. 1. The thermal decomposition curves of the chelating agent and metal chelates.
A. 2-Methyl-8-quinolinol
B. Scandium 2-methyl-8-quinolinol chelate
C. Uranium(VI) 2-methyl-8-quinolinol chelate
D. Thorium 2-methyl-8-quinolinol chelate
E. Yttrium 2-methyl-8-quinolinol chelate

Thorium. The thermal decomposition of the thorium 2-methyl-8-quinolinol chelate is shown in Fig. 1. This chelate was found to be the most stable of all the chelates studied. The normal chelate, $Th(C_{10}H_8NO)_4$, was stable up to 185°C where it began to decompose slowly. At 325°C, the decomposition began to proceed more rapidly, resulting in the ThO_2 level beginning at 435°C. From the results of this study and of a previous study[5], the 2-methyl-8-quinolinol chelate might successfully be used as a gravimetric procedure for the determination of thorium. This chelate would be preferred to that of the 8-quinolinol chelate because the latter begins to decompose at about 80°C[6].

Scandium. The thermal decomposition of the scandium 2-methyl-8-quinolinol chelate is shown in Fig. 1. The precipitated compound corresponded to the solvated chelate having the formula, $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_8NOH$. The first weight loss occurred at 70°C to give a break in the curve, but not a horizontal level, from 120 to 160°C. The composition of the compound in this region did not correspond to any known stoichiometry. A more rapid decomposition then began at 160°C to give a break in the curve at 225°C. The composition of the compound at 225°C corresponded closely to the formula for the normal chelate, $Sc(C_{10}H_8NO)_3$. However, this compound began to decompose slowly on further heating because a horizontal weight level was not found. Beyond 340°C, further decomposition took place to give the Sc_2O_3 level beginning at 660°C.

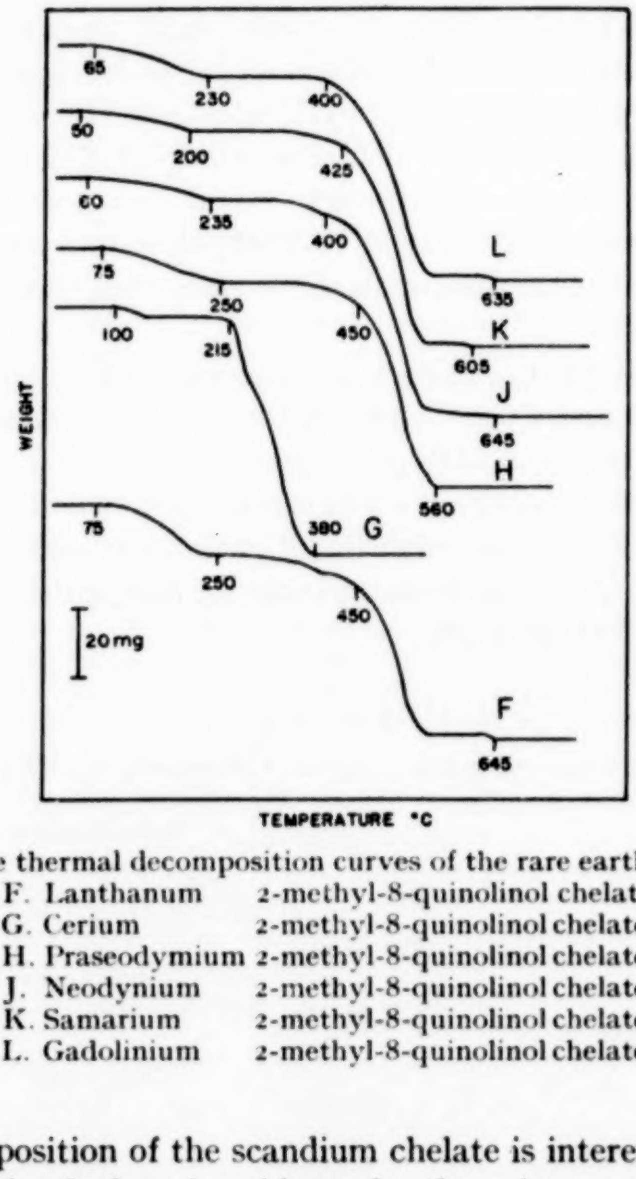

Fig. 2. The thermal decomposition curves of the rare earth chelates.

F. Lanthanum	2-methyl-8-quinolinol chelate
G. Cerium	2-methyl-8-quinolinol chelate
H. Praseodymium	2-methyl-8-quinolinol chelate
J. Neodynium	2-methyl-8-quinolinol chelate
K. Samarium	2-methyl-8-quinolinol chelate
L. Gadolinium	2-methyl-8-quinolinol chelate

The thermal decomposition of the scandium chelate is interesting in that contrary to the 8-quinolinol chelate[6], there is evidence for the existence of the normal chelate. Perhaps the normal chelate could be prepared by heating the solvated chelate at temperatures a little lower than 225°C.

Yttrium. The thermal decomposition of the yttrium 2-methyl-8-quinolinol chelate is shown in Fig. 1. The decomposition curve is similar, as might be expected, to the rare earth metal chelate decomposition curves in Fig. 2. The precipitated chelate, $Y(C_{10}H_8NO)_3$, was stable up to 65°C where it began to decompose slowly. At 425°C, the decomposition became more rapid resulting in the Y_2O_3 level beginning at 565°C. The yttrium chelate was much less stable than the 8-quinolinol chelate which began to decompose at 175°C[12].

Rare earth elements. The thermal decomposition curves of the 2-methyl-8-quinolinol chelates of lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium are shown in Fig. 2. In general, the decomposition curves are all similar in appearance except cerium. The cerium chelate will be discussed separately.

The rare earth metal chelates precipitated from solution as the normal chelates, $M(C_{10}H_8NO)_3$; where M is La, Pr, Nd, Sm and Gd. The air-dried chelates were stable up to 50 to 75°C where they began to decompose slowly. The rate of decomposition increased rapidly above 400 to 450°C giving the oxide levels in the temperature range of 560 to 645°C.

As contrasted to the 8-quinolinol chelates[12], the 2-methyl-8-quinolinol chelates decomposed at lower temperatures and cannot be recommended for the gravimetric determination of these elements. This, of course, might be expected as shown by the studies on the 2-methyl-8-quinolinol chelates with the divalent metal ions[7].

Cerium. The reaction between cerium(III) and 2-methyl-8-quinolinol, under the experimental conditions of this study, yielded an unexpected development. The reaction of the reagent with other trivalent rare earth metal ions gave yellow colored precipitates. However, with cerium(III), a purple colored precipitate was obtained. This would perhaps be indicative of the formation of a different type of chelate than with the other trivalent rare earth ions.

Previous work showed that this chelate corresponded to the formula, $Ce(C_{10}H_8NO)_4$[13]. Oxygen from the air oxidizes the Ce(III) to Ce(IV). A reaction of this type is also known to occur in the presence of 8-quinolinol[14].

The thermal decomposition of the cerium chelate is shown in Fig. 2. This chelate was the most stable of all of the rare earth metal chelates studied. The first weight loss occurred at 100°C. The decomposition was slow at first, but increased rapidly above 215°C to give the CeO_2 level at 380°C.

TABLE I

OBSERVATIONS ON METAL 2-METHYL-8-QUINOLINOL CHELATES

	Metal chelate	*Color*	*Chelate temperature limit °C*[a]	*Minimum oxide temperature limit °C*[a]
1.	$UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_8NOH$	orange	55	—
2.	$UO_2(C_{10}H_8NO)_2$	—	258—290	480
3.	$Th(C_{10}H_8NO)_4$	cream	185	435
4.	$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_8NOH$	yellow	70	—
5.	$Sc(C_{10}H_8NO)_3$	—	225—340	660
6.	$Y(C_{10}H_8NO)_3$	yellow	65	565
7.	$La(C_{10}H_8NO)_3$	yellow	65	645
8.	$Ce(C_{10}H_8NO)_4$	purple	100	380
9.	$Pr(C_{10}H_8NO)_3$	yellow	75	560
10.	$Nd(C_{10}H_8NO)_3$	yellow	60	645
11.	$Sm(C_{10}H_8NO)_3$	yellow	50	605
12.	$Gd(C_{10}H_8NO)_3$	yellow	65	635
13.	$C_{10}H_8NOH$	—		

[a] Heating rate of 4.5°C per minute.

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General observations on chelates. The minimum decomposition temperatures and minimum oxide level temperatures are listed in Table I. Preliminary solubility tests were conducted on the metal chelates in common organic solvents. It was found that they were slightly soluble in chloroform, acetonitrile, dioxane, acetone, $2N$ acetic acid and dilute mineral acids.

SUMMARY

The thermal decomposition of the 2-methyl-8-quinolinol (8-hydroxyquinaldine) chelates of scandium, thorium, uranium(VI), yttrium and the rare earth elements was studied on the thermobalance. It was found that the scandium and uranium(VI) chelates can lose the extra molecule of solvation by thermal decomposition. The thorium chelate was found to be the most stable of all the chelates studied. The temperature limits for the chelates and the minimum oxide level temperatures are given.

RÉSUMÉ

La décomposition thermique des chélates de la méthyl-2-hydroxy-8-quinoléine (hydroxy-8-quinaldine) avec le scandium, le thorium, l'uranium(VI), l'yttrium et les éléments des terres rares, a été étudiée sur la thermobalance. On a constaté que les chélates de scandium et d'uranium(VI) peuvent perdre leur molécule d'hydroxy-quinaldine supplémentaire de solvatation par décomposition thermique. Le chélate du thorium est le plus stable de tous les chélates étudiés. Les températures limites des chélates sont données, ainsi que les températures minimum au stade oxyde.

ZUSAMMENFASSUNG

Die thermische Zersetzung der 2-Methyl-8-Chinolinol (8-Oxychinaldin)-Chelate von Scandium, Thorium, Uran(VI), Yttrium und der seltenen Erden wurde auf der Thermowaage untersucht. Es wurde festgestellt, dass das Scandium- und das Uran(VI)-Chelat ihr 8-Oxychinaldin-Solvatationsmolekül durch thermische Zersetzung verlieren können. Das Thorium-Chelat war von allen untersuchten Chelaten das stabilste. Die Temperaturgrenzen für die Chelate und die Minimumtemperaturen für die Oxydstufen wurden mitgeteilt.

REFERENCES

[1] L. L. MERRITT AND J. K. WALKER, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 387.
[2] H. IRVING, E. J. BUTLER AND M. F. RING, *J. Chem. Soc.*, (1949) 1489.
[3] H. FRIESER, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, 14 (1953) 199.
[4] W. D. JOHNSTON AND H. FRIESER, *Anal. Chim. Acta*, 11 (1954) 201.
[5] J. P. PHILLIPS, J. F. EMERY AND H. P. PRICE, *Anal. Chem.*, 24 (1952) 1033.
[6] W. W. WENDLANDT, *Anal. Chem.*, 28 (1956) 499.
[7] M. BORREL AND R. PÂRIS, *Anal. Chim. Acta*, 5 (1951) 573.
[8] C. DUVAL, *Anal. Chem.*, 23 (1951) 1271.
[9] M. BORREL AND R. PÂRIS, *Anal. Chim. Acta*, 4 (1950) 267.
[10] G. BOCQUET AND R. PÂRIS, *Anal. Chim. Acta*, 14 (1956) 201.
[11] W. W. WENDLANDT, *Anal. Chem.*, 27 (1955) 1277.
[12] W. W. WENDLANDT, *Anal. Chim. Acta*, 15 (1956) 109.
[13] W. W. WENDLANDT, *J. Inorg. Nucl. Chem.*, 4 (1957) 133.
[14] T. I. PIRTEA, *Bul. chim. soc. române chim.*, 39 (1937-38) 83.

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GRAVIMETRIC DETERMINATION OF BARIUM IN ZIRCONIUM METAL AND IN CERTAIN ZIRCONIUM SALTS

by

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INTRODUCTION

Because of its favorable nuclear properties and its high resistance to corrosion by sodium, zirconium has been favored as the structural material in sodium-cooled high temperature atomic energy reactors.

Barium was first qualitatively detected in zirconium metal by spectrographic means. There existed a possibility that any barium which might be present in zirconium metal could be leached from the structural metal when immersed in hot sodium. This would accelerate the destruction of the zirconium metal. A study was undertaken to develop a reliable wet method for the determination of microgram-quantities of barium in zirconium, in order that the specific effect of hot sodium on zirconium metal could be determined.

Early attempts to determine barium spectrographically in the presence of zirconium had indicated high contents. No specific information has been published on the bulk separation of large amounts of zirconium from impurities, and only general knowledge was cited[1,2,3]. SEIDELL[4] listed the solubilities of zirconyl chloride in hydrochloric acid, but specific studies must be undertaken to determine the exact conditions of the optimum insolubility range of zirconyl chloride in mixtures of hydrochloric and hydrofluoric acid solutions. The schematic for the separation of barium from zirconium might also be extended as a general separation for determining other impurities in zirconium.

A gravimetric method for the determination of barium was preferred in order that all precipitates could be checked by X-ray fluorescence for zirconium and other impurities.

The most used methods for the gravimetric determination of barium are the sulfate and the chromate procedures[5]. The rhodizonate[6] and the 8-quinolinol[3] methods are too insensitive in the lower concentration ranges. The barium sulfate procedure was selected.

DEAL[7] precipitated barium with sulfuric acid in (1 to 1) hydrochloric acid solution (pH about 0.2). DEAL's results were just slightly high in the 0 5 to 2.5 mg range and no data were given for smaller quantities of barium.

The method developed here deals with the precipitation of barium as barium sulfate, in which excess ammonium sulfate is used as the precipitating agent in a hydrochloric acid medium after complete removal of the zirconium.

A schematic for the separation of barium from zirconium is shown in Fig. 1.

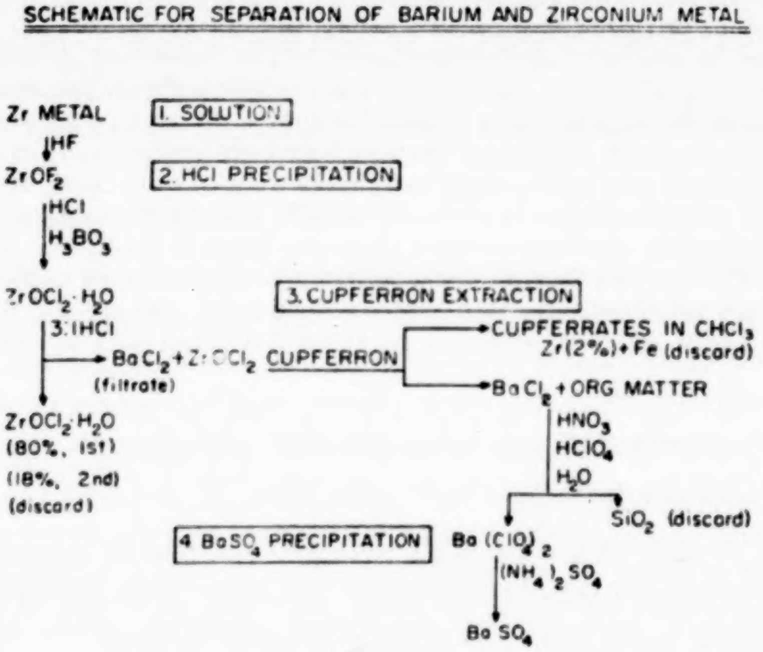

Fig. 1.

DETERMINATION OF BARIUM

Procedure

Hydrated zirconyl chloride. Dissolve 30 g of zirconyl chloride (30 g $ZrOCl_2 \cdot 8\,H_2O \hat{=} 8.5$ g Zr) with a minimum amount of water (30-35 ml) in a 150-ml beaker. Add twice the calculated amount of hydrochloric acid (40 ml) to precipitate the zirconium as zirconyl chloride. Evaporate with caution to about 5 ml over an asbestos gauze. Adjust the acidity to (3 : 1) hydrochloric acid and the total volume to 20 ml by the addition of 2.5 ml water and 12.5 ml of concentrated hydrochloric acid. Cool in an ice-bath. Filter through a 125-ml "medium" sintered glass funnel using suction. Wash with a minimum amount of cold (3 : 1) hydrochloric acid. (The residue may be dried at 55° and considered as purified zirconyl chloride.) Transfer the filtrate to a 150-ml beaker with water, and evaporate to a small volume (approximately 5 ml). Add 5.0 ml of concentrated hydrochloric acid. The solution is now (3 : 1) hydrochloric acid in a total volume of 10 ml. Cool slightly in an ice bath. Filter through a 60-ml "medium" sintered glass funnel. Wash with a minimum of cold (3 : 1) hydrochloric acid. Transfer the solution to a 500-ml separatory funnel with water. Make the solution 10% in hydrochloric acid by the addition of 15 ml of hydrochloric acid, 75 ml of water, and 100 ml of aqueous 6% cupferron solution. Mix. Add 100 ml of chloroform and shake for 2 to 3 minutes. Allow to separate; drain off the lower chloroform layer and discard. (If the previous precipitate was heavy, perform an additional extraction: add 5 ml of concentrated hydrochloric acid, 50 ml of 6% cupferron solution and 100 ml of chloroform, shake 2 to 3 minutes and discard the lower chloroform layer.) One extraction is usually sufficient. A green color in the water solution indicates decomposition products of cupferron. Add 100 ml of chloroform; shake and discard the final organic layer. Transfer the virtually zirconium-free, iron-free filtrate to a 600-ml beaker and evaporate to half-volume. Add 100 ml nitric acid and evaporate to half-volume again. Add 25 ml more of nitric acid and 15 ml of perchloric acid. Fume to near-dryness. Cool. Add 50 ml of water, boil gently for 5 minutes and filter into a 600-ml beaker. Wash with hot 2% hydrochloric acid. Discard the residue. Dilute the filtrate to 150 ml. Neutralize with (1 to 1) ammonium hydroxide; adjust the pH to 0.65 with (1 to 1) hydrochloric acid. Heat to boiling and add 15 ml of a fresh 50% ammonium sulfate solution dropwise with stirring. Mark the volume with a marking pencil. Boil gently 15 to 20 minutes, adjust the volume to the mark and add 15 ml more of 50% ammonium sulfate. Boil gently until fine barium sulfate crystals coagulate and settle. Maintain the original volume by the addition of water. Allow the sample to stand overnight, if possible. Filter by decantation through a No. 42 Whatman 12.5-cm filter paper using paper pulp. Transfer the final residue to the filter paper. Wash with hot water containing 1% ammonium sulfate and 0.1% sulfuric acid. Transfer the paper containing barium sulfate to a porcelain crucible. Dry, char, ignite at 850°C, cool and weigh. Calculate per cent barium.

The filter paper blank averages 0.12 mg.

Zirconium metal

Weigh a 10-gram sample of zirconium metal chips and place in a large platimum evaporating dish. Add enough water (approximately 10 ml) to completely immerse the metal. Add a total of 25 ml of hydrofluoric acid dropwise from a small polyethylene bottle with an occasional addition of several ml of water to prevent crystal formation. Heat to evolve excess hydrofluoric acid; evaporate to incipient crystallization. Add twice the theoretical amount of concentrated hydrochloric acid to precipitate the zirconium as zirconyl chloride. (About 40 ml of concentrated hydrochloric acid are required per 10 g zirconium metal.) Calculate the amount of boric acid necessary to combine with the hydrofluoric acid. (Approximately 12 g of boric acid are required per 25 ml hydrofluoric acid.) Add the solid boric acid to the sample and slowly evaporate the entire sample to a small volume. Evaporate over an asbestos gauze to prevent bumping. Wash down the sides with a small amount of water and continue evaporating to a volume of approximately 5 ml. Add 2.5 ml of water plus 12.5 ml of concentrated hydrochloric acid, making the total volume 20 ml of a (3 to 1) hydrochloric acid solution. Proceed as under hydrated zirconyl chloride.

EXPERIMENTAL RESULTS AND DISCUSSION

Bulk separation of zirconyl chloride

Zirconyl chloride octa-hydrate crystals dissolve readily in water, but are slightly less soluble in concentrated hydrochloric acid. In order to re-precipitate the dissolved zirconium, hydrochloric acid was added in a limited volume.

TABLE I

SOLUBILITY OF ZIRCONIUM

(5.0 g $ZrOCl_2 \cdot 8\,H_2O$ (1.42 g Zr) USED

$HCl:H_2O$	*Total volume*	*Zr in g*	
		soluble	*insoluble*
0 : 30	30	1.42	none
1 : 2	30	1.42	none
1 : 1	30	0.39	1.03
1 : 1	30	0.33	1.09
2 : 1	30	0.21	1.21
3 : 1	30	0.20	1.22
3 : 1	30	0.14	1.28
30 : 0	30	0.67	0.75
(1 : 1)	(10)	(0.10)	(1.32)

A series of solubility tests were made (Table I) in which 5 g of zirconyl chloride were dissolved in selected concentrations of hydrochloric acid in order to find the optimum point of insolubility. Optimum insolubility occurred in a (3 to 1) hydrochloric acid medium, where only 0.14 to 0.20 g of zirconium remained in solution. As much as 80% of the zirconium was removed by filtration. X-ray diffraction patterns indicated that a fairly pure hydrated zirconyl chloride was removed in this first separation. Chemical analysis of the precipitate approximated a quinque-hydrate[2]. The second filtration removed all but about 0.25 g of the zirconium salt. X-ray diffraction patterns of this last separated salt indicated the formation of still another hydrated zirconyl chloride and chemical analysis showed 11 to 12 molecules of water.

Cupferron separation

The residual zirconium and any interfering quantities of iron were precipitated with cupferron and extracted and removed with chloroform[8]. In order to insure complete separation of the zirconium, the acidity was adjusted to 10% hydrochloric acid before the cupferron extraction and quantities of 6 g or of 6 and 3 g of cupferron in solution were added, respectively. A determination of zirconium in the filtrate[9] indicated that a residual of 10 μg or less may be expected. The final filtrate was virtually iron-free and zirconium-free[8].

After fuming with nitric and perchloric acids, a rapid filtration removed any silica.

Precipitation of barium as barium sulfate

Preliminary studies were made in water solution to determine the optimum conditions for the gravimetric determination of small amounts of barium.

From a series of synthetic solutions in which the barium concentration was varied from 0.5 to 3.0 mg, extremely high results were obtained when sodium sulfate was used as a precipitating agent. The differences in mg Ba added and recovered ranged from 2.9 to 7.2 mg. These results indicated coprecipitation of the sodium salts. When small volumes of (1 to 1) sulfuric acid solution were added in a similar series, the results were slightly low; as much as —0.3 mg loss in barium was noted in the 2.0-mg synthetic solution. When the added volume of (1 to 1) sulfuric acid solution was increased to 10 ml, no improvement in the recovery of the barium was noted. Results were still low.

Further study indicated that when a sufficiently large amount of ammonium sulfate was used as precipitating reagent for barium, complete recovery of the barium resulted. The variation of solution pH from 0.0 and 1.4 produced no large differences, except, that when a pH just above one was maintained a tendency toward a more complete recovery of the barium was noted. 5-g and 10-g portions of ammonium sulfate proved inadequate[10], but when the amount of ammonium sulfate precipitant was increased to 15 g in a slightly acid medium (pH 1.0) very satisfactory recovery of milligram-quantities of barium resulted. By adjusting the pH of the prepared (zirconium-free, iron-free) solution to 0.65 and by maintaining the same volume of solution after the addition of the 15 g ammonium sulfate, a pH of about 1.0 would be maintained. The addition of ammonium sulfate in two separate portions together with gentle boiling formed an easily filterable barium sulfate.

Barium in zirconyl chloride

In a series of samples, zirconyl chloride was varied from 0 to 30 g and the sample analyzed for barium. Impure zirconyl chloride crystals contained an average of 0.015% barium as such or 0.055% barium in terms of zirconium metal (Table II, No. 2-4). In a second series of samples, using purchased "purified" zirconyl chloride, five 30-g samples of the "as received" material were analyzed for barium. This purchased purified-grade zirconyl chloride contained an average of 0.004% barium or 0.016% barium when calculated in terms of zirconium metal (Table II, No's. 5-9).

To 30-g portions of zirconyl chloride recovered as *residue* in this proposed analytical procedure, were added 0, 0.2, and 1.0 mg of barium, respectively; 0.1, 0.3, and 1.0 mg of barium were recovered. This affords evidence that the zirconyl chloride *residues* do not entrain barium and are, therefore, free of barium.

Barium in zirconium metal

Available samples of zirconium metal were also analyzed for barium (Table III).

TABLE II

DETERMINATION OF BARIUM IN ZIRCONIUM

No.	Source	$ZrOCl_2$ g	Equivalent Zr g	Ba added mg	Ba found mg	Ba in $ZrOCl_2$ %	Ba as if in Zr %
1.	Blank	0.0	0.0	0.0	0.0		
2.	Impure[a]	5.0	1.4	0.0	0.9	0.018	0.063
3.	,,	15.0	4.3	0.0	2.3	0.015	0.054
4.	,,	30.0	8.5	0.0	4.0	0.013	0.047
5.	Purified[a]	30.0	8.5	0.0	1.5	0.005	0.018
6.	,,	30.0	8.5	0.0	1.3	0.004	0.015
7.	,,	30.0	8.5	0.0	1.4	0.005	0.016
8.	,,	30.0	8.5	0.0	1.2	0.004	0.014
9.	,,	30.0	8.5	0.0	1.3	0.004	0.015
10.	1st separation of a "Purified"[b]	24.0	8	0.0	0.1	0.000	0.001
11.	,,	24.0	8	0.2	0.3	0.001	0.004
12.	,,	24.0	8	1.00	1.0	0.004	0.013

[a] g $ZrOCl_2 \cdot 8\ H_2O$ used as starting material

[b] g $ZrOCl_2 \cdot 5\ H_2O$ used as starting material

Crystal bar zirconium contained 0.000 and 0.001% barium, zirconium tubing contained 0.001%, and structural zirconium metal sheet contained 0.003 and 0.004% barium.

When a known amount of barium was added to the structural sheet, barium was recovered ± 0.001% (Table III, No. 5). The deviation is ± 0.1 mg of barium.

X-ray fluorescence analysis of the final barium sulfate residue showed complete separation of the zirconium, and absence of other impurities.

TABLE III

DETERMINATION OF BARIUM IN ZIRCONIUM METAL

No.	Type Zr	Zr metal g	Ba added mg	Ba found mg	Ba %
1.	Crystal bar	10.00	0.0	0.0	0.000
2.	,, ,,	10.00	0.0	0.1	0.001
3.	Tubing	10.00	0.0	0.1	0.001
4.	Sheet	10.14	0.0	0.4	0.004
5.	,,	10.12	0.0	0.3	0.003
5a.	,,	10.14	1.0	1.3	0.013

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SUMMARY

Barium may be determined gravimetrically in quantities ranging from 0.2 to 2.0 mg (± 0.1 mg) in hydrated zirconyl chloride and in zirconium metal after complete separation of the zirconium. As much as 10 g of zirconium may be removed by a double precipitation in a (3 to 1) hydrochloric acid medium followed by a cupferron precipitation-chloroform extraction of the residual zirconium. The barium is then determined gravimetrically as barium sulfate in the iron-free, zirconium-free filtrate by precipitation with an excess of ammonium sulfate. As much as 0.015% barium has been found in impure zirconyl chloride, 0.004% in commercial "purified" zirconyl chloride, 0.000% barium in crystal bar zirconium metal and 0.003% barium in zirconium metal sheet. Reproducibility is 0.001%.

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RÉSUMÉ

Le baryum peut être dosé gravimétriquement en quantités allant de 0.2 à 2.0 mg (± 0.1 mg), dans le chlorure de zirconyle hydraté, et dans le zirconium métallique, après complète séparation du zirconium. On peut éliminer jusqu'à 10 g de zirconium par double précipitation dans l'acide chlorhydrique (3 : 1), et ensuite par précipitation au moyen de cupferron et extraction au chloroforme du zirconium restant. Le baryum est finalement dosé gravimétriquement comme sulfate de baryum dans le filtrat (exempt de fer et de zirconium), au moyen d'un excès de sulfate d'ammonium. On a décelé jusqu'à 0.015% de baryum dans un chlorure de zirconyle impur, 0.004% dans un chlorure de zirconyle commercial ,,purifié'', 0.000% dans le zirconium métallique cristallisé, en barres, et 0.003% dans le zirconium en feuille. Reproductibilité : 0.001%.

ZUSAMMENFASSUNG

Das Barium kann gravimetrisch in Mengen von 0.2 bis 2.0 mg (0.1 mg) in hydratiertem Zirkonylchlorid und in Zirkoniummetall nach vollständiger Abtrennung des Zirkoniums bestimmt werden. Bis zu 10 g Zirkonium können durch doppelte Fällung in einem salzsauren (3 zu 1) Milieu, gefolgt von Cupferronfällung-Chloroformextraktion des noch vorhandenen Zirkoniums, entfernt werden. Das Barium wird dann gravimetrisch als Bariumsulfat in dem eisenfreien, zirkoniumfreien Filtrate durch Fällung mit überschüssigem Ammoniumsulfat bestimmt. Bis zu 0.015% Barium wurde in unsauberem Zirkonylchlorid gefunden, 0.004% in einem ,,gereinigten'' Handelsprodukt von Zirkonylchlorid, 0.000% Barium in kristallisiertem Zirkoniummetall in Stangen und 0.003% Barium in Zirkoniummetall in Blättern. Reproduzierbarkeit 0.001%.

REFERENCES

[1] F. P. VENABLE, *Zirconium and Its Compounds*, Rheinhold Pub. Corp., New York, 1922, Chap. II, p. 22.
[2] F. P. VENABLE, *ibid.*, p. 66.
[3] B. A. J. LISTER AND L. A. MCDONALD, *J. Chem. Soc.*, (1952) 4315.
[4] A. SEIDELL, *Solubilities of Inorganic and Metal Organic Compounds*, Vol. 1, 3rd ed., D. Van Nostrand Co., Inc., New York, 1940, p. 1597.
[5] I. M. KOLTHOFF AND E. B. SANDELL, *Textbook of Quantitative Inorganic Analyses*, 3rd ed., Macmillan Co., New York, 1952, Chap. XX, p. 326.
[6] F. FEIGL, *Spot Tests*, Vol. I, 4th ed., Elsevier Pub. Co., New York, 1954, p. 203.
[7] S. B. DEAL, *Anal. Chem.*, 27 (1955) 109.
[8] N. H. FURMAN, W. B. MASON AND J. S. PEKOLA, *Anal. Chem.*, 21 (1949) 1325.
[9] L. SILVERMAN AND D. W. HAWLEY, *Anal. Chem.*, 28 (1956) 806.
[10] K. TAKAGI, *J. Chem. Soc. Japan, Chem. Sect.*, 72 (1951) 364; *C.A.*, 46 (1952) 854a.

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SODIUM METAVANADATE AS VOLUMETRIC REAGENT

V. DETERMINATION OF ORGANIC DERIVATIVES OF HYDRAZINE, IODINE MONOCHLORIDE METHOD

by

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The nature and proportions of the end-products of the oxidation of hydrazine and its derivatives vary with the specific nature and the oxidation-reduction potential of the oxidising system and with the pH of the medium. BROWNE[1] found that hydrogen peroxide reacted with hydrazine to form hydrogen azide. BROWNE AND SHATTERLY[2] studied the action of a number of oxidising agents upon hydrazine. In most cases nitrogen was the primary product and under certain conditions ammonia and hydrogen azide were also produced as a result of the secondary reaction. EMIL FISCHER[3] stated that an emulsion of phenylhydrazine and water reacted with iodine as follows:

$$2\ C_6H_5NH{\cdot}NH_2 + 2\ I_2 = C_6H_5NH_2{\cdot}HI + C_6H_5N_3 + 3\ HI$$

According to E. VON MEYER[4] if an excess of phenylhydrazine is used the reaction that occurs is:

$$C_6H_5NH{\cdot}NH_2 + 2\ I_2 = C_6H_5I + 3\ HI + N_2$$

Fehling's solution oxidises phenylhydrazine to benzene, water and nitrogen; and the gasometric method of WATSON SMITH[5] is based on this reaction. According to KURTENACKER AND KUBINA[6] direct titration of phenylhydrazine and semicarbazide with iodate to the iodine monochloride end-point is possible. MILLER AND FURMAN[7] have shown that the oxidation of phenylhydrazine in acidic solution by potassium iodate in presence of mercuric ions results in the formation of diazonium salt which slowly hydrolyses giving off nitrogen and forming phenol. They have also suggested that the rapid reaction of semicarbazide with iodate in acid solution is not due to hydrolysis, but depends upon direct attack of the hydrazine group with intermediate formation of unstable carbamic acid, which immediately breaks down to give carbon dioxide and ammonia. According to BRITTON AND CLISSOLD[8], phenylhydrazine on oxidation with cupric ions or with Fehling's solution yields benzene and phenol. SINGH *et al.*[9] have shown that the oxidation of hydrazine with potassium metaperiodate to iodine monochloride and iodine bromide end-point respectively gives nitrogen. SINGH *et al.*[10] have also used chloramine-B, chloramine-T, sodium metavanadate and diethylene tetraammonium sulphatocerate in hydrochloric acid medium for the oxidation of hydrazine to nitrogen and water with a four-electron change:

$$N_2H_4 + 2\ O = N_2 + 2\ H_2O$$

MCBRIDE, HENRY AND SKOLNIK[11] have shown that the hydrazino group in monosubstituted hydrazines, their hydrazones and acyl derivatives, is oxidised with a four-electron change to nitrogen with potassium iodate in both hydrochloric and sulphuric acid solutions. The reduction of iodate takes place to iodine monochloride in hydrochloric acid and to iodine in sulphuric acid.

$$H_2H_5^+ + IO_3^- + H_3O^+ + Cl^- = ICl + N_2 + 4\ H_2O$$

$$5\ N_2H_5^+ + 4\ IO_3^- = 5\ N_2 + 11\ H_2O + H_3O^+ + 2\ I_2$$

In the present investigation sodium metavanadate has been used for the volumetric determination of semicarbazide hydrochloride, benzalazine, benzal semicarbazone, aminoguanidine hydrochloride, chloralhydrazine, *o*-hydroxybenzal semicarbazone, *p*-methoxybenzalsemicarbazone, *o*-chlorobenzalsemicarbazone and ethyl methyl ketone semicarbazone. In presence of hydrochloric acid these derivatives of hydrazine react with sodium metavanadate in accordance with the equations:

$$4\ VO_3^- + NH_2CONH{\cdot}NH_2 + 12\ H^+ = 4\ VO^{+2} + CO_2 + NH_3 + N_2 + 7\ H_2O$$

$$4\ VO_3^- + (C_6H_5CH{:}N\text{-})_2 + 12\ H^+ = 4\ VO^{+2} + 2\ C_6H_5CHO + N_2 + 6\ H_2O$$

$$4\ VO_3^- + C_6H_5CH{:}N{\cdot}NHCONH_2 + 12\ H^+ = 4\ VO^{+2} + C_6H_5CHO + CO_2 + NH_3 + N_2 + 6\ H_2O$$

$$4\ VO_3^- + HN{:}C(NH{\cdot}NH_2)NH_2 + 12\ H^+ = 4\ VO^{+2} + HN{:}C(OH)NH_2 + N_2 + 7\ H_2O$$

$$4\ VO_3^- + C{:}Cl_3CH(OH)NH{\cdot}NH_2 + 12\ H^+ = 4\ VO^{+2} + CCl_3CH(OH)_2 + N_2 + 7\ H_2O$$

$$4\ VO_3^- + HO{\cdot}C_6H_4CH{:}N{\cdot}NHCONH_2 + 12\ H^+ = 4\ VO^{+2} + HO{\cdot}C_6H_4CHO + CO_2 + NH_3 + N_2 + 6\ H_2O$$

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$$4\,VO_3^- + CH_3O{\cdot}C_6H_4CH{:}NNHCONH_2 + 12\,H^+ = 4\,VO^{+2} + CH_3O{\cdot}C_6H_4CHO + CO_2 + NH_3 + N_2 + 6\,H_2O$$

$$4\,VO_3^- + Cl{\cdot}C_6H_4CH{:}N{\cdot}NHCONH_2 + 12\,H^+ = 4\,VO^{+2} + Cl{\cdot}C_6H_4CHO + CO_2 + NH_3 + N_2 + 6\,H_2O$$

$$4\,VO_3^- + C_2H_5(CH_3)C{:}N{\cdot}NHCONH_2 + 12\,H^+ = 4\,VO^{+2} + C_2H_5COCH_3 + CO_2 + NH_3 + N_2 + 6\,H_2O$$

EXPERIMENTAL

A known amount of the hydrazine derivative was taken in a conical flask and about 25 ml of water, 55 ml of conc. hydrochloric acid, 5 ml of 0.02*M* iodine monochloride and 5 ml of chloroform were added to it. The mixture was cooled to room temperature and titrated against 0.1*M* sodium metavanadate solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale green and the chloroform layer acquired a purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the metavanadate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The metavanadate solution was then added dropwise, with shaking after the addition of each drop, until the chloroform layer became light pale yellow. The end-point was very sharp.

In these titrations, normality of the solution with respect to hydrochloric acid was kept between 7*N* to 7.5*N*. Several titrations were performed in each case. From the volume of sodium metavanadate used corresponding to the end-point in each titration, the amount of each substance was calculated. The results showed that 0.02 to 0.12 g of the substances as listed above can be determined by using sodium metavanadate as an oxidising agent.

SUMMARY

Sodium metavanadate has been used as an oxidising agent in hydrochloric acid medium for the volumetric determination of semicarbazide hydrochloride, benzalazine, benzalsemicarbazone, aminoguanidine hydrochloride, *o*-hydroxybenzalsemicarbazone, *p*-methoxybenzalsemicarbazone, chloralhydrazine, *o*-chlorobenzalsemicarbazone and ethyl methyl ketone semicarbazone, using iodine monochloride as a catalyst and preoxidiser. Chloroform was used as an indicator. It was coloured violet due to the liberation of iodine during the titration and became light pale yellow at the end-point owing to the formation of iodine monochloride. Each hydrazino group in these compounds was oxidised quantitatively with a four-electron change to nitrogen with sodium metavanadate as an oxidant in hydrochloric acid solution.

RÉSUMÉ

Le métavanadate de sodium a été utilisé comme oxydant en milieu chlorhydrique pour le dosage volumétrique des composés suivants: chlorhydrate de semicarbazide, benzalazine, benzalsemicarbazone, chlorhydrate d'aminoguanidine, *o*-hydroxybenzalsemicarbazone, *p*-méthoxybenzalsemicarbazone, chloralhydrazine, *o*-chlorobenzalsemicarbazone et éthylméthylcétosemicarbazone, en utilisant le monochlorure d'iode comme catalyseur et ,,préoxydant''. Le chloroforme est utilisé comme indicateur; il se colore en violet par l'iode libéré au cours du titrage et devient jaune pâle au point final par formation de monochlorure d'iode. Chaque groupement ,,hydrazino'' dans ces composés est oxydé quantitativement, avec échange de 4 électrons entre l'azote et le métavanadate de sodium.

ZUSAMMENFASSUNG

Natriummetavanadat wurde in salzsaurem Milieu als Oxydationsmittel für die volumetrische Bestimmung von Semicarbazidhydrochlorid, Benzalazin, Benzal-semicarbazon, Aminoguanidinhydrochlorid, *o*-Oxybenzal-semicarbazon, *p*-Methoxybenzal-semicarbazon, Choralhydrazin, *o*-Chlorobenzal-semicarbazon und Methyläthylketon-semicarbazon mit Jodmonochlorid als Katalysator und Voroxydationsmittel verwendet. Chloroform wurde als Indikator benützt. Es wurde während der Titration durch die Freimachung von Jod violett gefärbt und wurde am Endpunkt schwach gelb durch Bildung von Jodmonochlorid. Alle Hydrazingruppen der genannten Verbindungen wurden im Laufe einer Vier-Elektronen-Umsetzung quantitativ mit Natriummetavanadat als Oxydationsmittel in salzsaurer Lösung zu Stickstoff oxydiert.

REFERENCES

[1] A. W. BROWNE, *J. Am. Chem. Soc.*, 27 (1905) 551.
[2] A. W. BROWNE AND F. F. SHATTERLY, *J. Am. Chem. Soc.*, 29 (1907) 1305; 30 (1908) 53; 31 (1909) 221, 783.
[3] EMIL FISCHER, *Ber.*, 10 (1887) 1335.
[4] E. VON MEYER, *J. prakt. Chem.*, 36 (1887) 115.
[5] WATSON SMITH, *Chem. News*, 93 (1906) 83.
[6] A. KURTENACKER AND H. KUBINA, *Z. anal. Chem.*, 64 (1924) 388.
[7] C. O. MILLER AND N. H. FURMAN, *J. Am. Chem. Soc.*, 59 (1937) 161.
[8] H. T. S. BRITTON AND E. M. CLISSOLD, *J. Chem. Soc.*, (1942) 528.
[9] B. SINGH *et al.*, *J. Indian Chem. Soc.*, 29 (1952) 34; *Anal. Chim. Acta*, 9 (1953) 22.
[10] B. SINGH *et al.*, *Anal. Chim. Acta*, 11 (1954) 313; 13 (1955) 301; 10 (1954) 408; 14 (1956) 109.
[11] WILLIAM R. MCBRIDE, RONALD A. HENRY AND SOL SKOLNIK, *Anal. Chem.*, 25 (1953) 1042.

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VOLUMETRIC IODATE METHOD FOR THE DETERMINATION OF THIOCYANATE

by

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Quantitative oxidation of thiocyanate by potassium iodate has been studied by various workers. JAMIESON[1] estimated copper by titrating the precipitated CuSCN with iodate to the iodine monochloride end-point in about half the final volume of concentrated hydrochloric acid. Similar procedures for the determination of zinc[2] and mercury[3], based upon the titration of $Zn[Hg(SCN)_4]$, were later proposed. LANG[4] recommended the use of excess iodate for the oxidation of thiocyanate in acid medium, the excess being determined iodometrically by thiosulphate. While a direct titration against KIO_3 in one-third to one-half the volume of hydrochloric acid to the iodine monochloride or the iodine cyanide end-point also yielded trustworthy results, a prior addition of ICl or ICN to thiocyanate was preferred to save its atmospheric oxidation[5]. In an electrometric investigation, FENWICK[6] reported good results for the estimation of thiocyanate by regulating the final HCl concentration near about 10%. According to HAMMOCK and co-workers[7], the high acidity in the iodate method causes a partial decomposition of SCN^- and for greater accuracy they suggest the addition of thiocyanate to iodine monochloride solution before commencing the titration. Concurrent studies by GAUGUIN[8], however, reveal that quantities of thiocyanate exceeding 10^{-4} g can be determined correctly in a minimum 1 N HCl by a direct potentiometric titration with iodate. Since such divergent views are expressed in the literature, a reinvestigation of the SCN^--IO_3^- reaction was considered desirable. The present paper describes the optimum conditions for an accurate determination of thiocyanate by standard KIO_3 using both the visual and the electrometric end-points.

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EXPERIMENTAL

The thiocyanate solution obtained by dissolving extra pure crystals of KSCN or NH_4SCN in water, was standardised by the classical Volhard method. A standard solution of KIO_3 was prepared from the E. Merck's guaranteed sample dried previously at 120°C for an hour. The following procedures were adopted for the estimation of thiocyanate:

A. Carbon tetrachloride indicator. To an aliquot volume of thiocyanate solution taken in a 350 ml glass-stoppered Erlenmeyer flask, 5 ml carbon tetrachloride and sufficient concentrated hydrochloric acid to make its final overall normality approximately $2N$ were added. The titration was performed against standard KIO_3 with constant swirling of the solution until the violet colour from the immiscible solvent vanished completely. The amount of thiocyanate in a given solution was determined from the equation

$$2\,KSCN + 3\,KIO_3 + 4\,HCl \rightarrow 2\,K_2SO_4 + KCl + 2\,HCN + 3\,ICl + H_2O.$$

Thus 1 ml of $1M$ KIO_3 is equivalent to 0.06479 g KSCN. Experimental results are given in Table I.

B. Electrometric end-point. A Cambridge direct-reading potentiometer was employed in the present series of experiments in conjunction with platinum and saturated calomel as the indicator and the reference electrodes respectively. A sensitive galvanometer served as the null point instrument. The titration vessel was a tall 250 ml beaker with the usual stirring arrangements. An aliquot portion of thiocyanate solution and enough HCl (as in method A) were transferred to the beaker and the e.m.f. was measured. During the titration with standard KIO_3 solution a characteristic potential

TABLE I

Overall normality of HCl = $\sim 2N$

Determination of KSCN		% Error
By Volhard's g	*By KIO_3* g	
0.007773	0.007785	0.15
0.01555	0.01555	0.00
0.02726	0.02724	0.08
0.03110	0.03105	0.16
0.05450	0.05442	0.15
0.06219	0.06220	0.01
0.09328	0.09330	0.02
0.1244	0.1244	0.00
(0.007773	0.007785	0.15)
(0.01555	0.01557	0.13)
(0.03110	0.03120	0.32)
(0.06219	0.06220	0.01)

TABLE II

EFFECT OF HCl CONCENTRATION ON THE $KSCN$-KIO_3 REACTION

10 ml $0.0320N$ KSCN taken each time

Final HCl concentration (N)	*Strength of KIO_3 (M)*	*Volume of KIO_3 required (ml)*		
		Theoretical	*CCl_4 indicator*	*Potentiometric end-point*
0.3	0.02462	19.50	19.85	—
0.8	0.02462	19.50	19.65	19.65
1.5	0.02462	19.50	19.45	19.45
1.7	0.03441	13.95	13.95	13.95
2.0	0.03441	13.95	13.95	13.95
2.5	0.02462	19.50	19.50	19.50
3.0	0.02462	19.50	19.50	19.50
4.0	0.02462	19.50	18.80	18.80
5.0	0.02462	19.50	18.10	18.10

break corresponding to the maximum of the derivative $\Delta E/\Delta V$ marked the end-point. Care was taken to perform the titration rapidly with vigorous stirring especially towards the end. A representative set of results is recorded in the parentheses of Table I. It will be seen that the amount of thiocyanate calculated by the present method is in fair agreement with that obtained by the standard. Identical results were obtained for the estimation of ammonium thiocyanate.

A series of experiments were first performed to examine the influence of hydrochloric acid concentration on the stoicheiometry of the SCN^--IO_3^- reaction. The data recorded in Table II show that accurate and reproducible results may be obtained by regulating the final acidity of the system between 1.5 and 3*N*. Whereas at low HCl concentrations the values were high, owing perhaps to the slight hydrolysis of iodine monochloride, with acidities beyond 3*N* a negative error was observed, due presumably to the partial decomposition and/or atmospheric oxidation of thiocyanate.

Potassium iodate is available in a very pure form and its solutions are perfectly stable for long durations[9]. Its utility as a primary standard in the direct determination of thiocyanate offers therefore a distinct advantage.

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SUMMARY

Direct titration of thiocyanate with standard potassium iodate solution is found to yield accurate results in a final hydrochloric acid concentration regulated between 1.5 and 3*N*. The end-point is determined either potentiometrically or with carbon tetrachloride indicator.

RÉSUMÉ

Le titrage direct du thiocyanate au moyen d'une solution étalon d'iodate de potassium fournit des résultats précis, si la concentration finale de l'acide chlorhydrique est maintenue entre 1.5et 3*N*. Le point final est déterminé soit par potentiométrie, soit en utilisant le tétrachlorure de carbone comme indicateur.

ZUSAMMENFASSUNG

Die direkte Titration von Thiocyanat mit Kaliumjodat-Titerlösung gibt genaue Resultate wenn man die Endkonzentration der Salzsäure zwischen 1.5 und 3*N* hält. Der Endpunkt wird entweder potentiometrisch oder mit Tetrachlorkohlenstoff als Indikator bestimmt.

REFERENCES

[1] G. S. Jamieson, L. H. Levy and H. L. Wells, *J. Am. Chem. Soc.*, 30 (1908) 760.
[2] G. S. Jamieson, *Am. J. Sci.*, 33 (1912) 349.
[3] G. S. Jamieson, *J. Am. Chem. Soc.*, 40 (1918) 1036.
[4] R. Lang, *Z. anorg. u. allgem. Chem.* 142 (1925) 290.
[5] W. Böttger, *Newer Methods of Chemical Analysis*, Chapman and Hall Ltd., London, 1938, p. 67.
[6] F. Fenwick, in I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, J. Wiley & Sons, Inc., New York, 1949, p. 300.
[7] E. W. Hammock, D. Beavons and E. H. Swift, *Anal. Chem.*, 21 (1949) 970.
[8] R. Gauguin, *Anal. Chim. Acta*, 3 (1949) 272.
[9] I. M. Kolthoff, *Volumetric Analysis*, Vol. II, J. Wiley & Sons, Inc., New York, 1929, p. 456.

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THE DETERMINATION OF PARATHION VAPOUR AND DUST IN THE ATMOSPHERE

by

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Published methods for the microdetermination of diethyl *p*-nitrophenyl phosphorothionate (parathion, E605) have been based on ultraviolet absorption[1], or on colorimetry after conversion to *p*-nitrophenol[2], after reduction to the amino compound followed by conversion to an azo dye[3,4], or after oxidation to inorganic phosphate[5]. Any of these methods can be used in the determination of traces of parathion in the atmosphere if a suitable sampling technique is available; one published method[2] makes use of an observation, originating in this laboratory, that filter paper not only traps parathion mist and dust, but also adsorbs parathion vapour. The sensitivity of this method may be increased many times if the parathion collected on the paper is subjected to reduction and conversion to an azo dye, rather than to hydrolysis to *p*-nitrophenol; an observation that parathion may rapidly be reduced at room temperature by means of a zinc-copper couple has allowed this increased sensitivity to be gained without much increase in the complexity of the method. The zinc-copper couple is prepared *in situ* by adding a drop of copper sulphate solution to an acid solution of parathion containing zinc dust in suspension.

Experiment has shown that parathion vapour and dust may also be efficiently trapped in a short cellulose powder column, and a further simplification of the method may be attained by incorporating zinc dust in the cellulose powder and reducing the parathion before elution.

METHOD

Reagents

Copper sulphate solution — A 2% w/v solution of hydrated cupric sulphate, $CuSO_4 \cdot 5H_2O$, in distilled water.

Sodium nitrite solution — A 0.25% w/v solution of sodium nitrite in distilled water; this should be prepared freshly each week and stored in the refrigerator.

*N-Sulphatoethyl-*m*-toluidine solution* — A 2% w/v solution of the pure white solid in distilled water; this solution should preferably be stored in the refrigerator and should be discarded if it becomes discoloured.

Collection of air sample

Whatman filter paper — Insert three sheets of Whatman No. 1 filter paper in a test paper holder[2] and connect the assembled apparatus to a suction pump capable of drawing air through the paper at a constant rate of 5 l per min. The preferred method in this laboratory is the use of a centrifugal electric vacuum pump in conjunction with a calibrated orifice plate. Aspirate sufficient of the atmosphere to be tested through the paper to collect about 20 μg parathion. Remove the papers carefully from the holder and place the first two without folding in a 250 ml conical flask. The third paper, which acts as a control to ensure that no parathion is passing the first two, is introduced into a similar flask. Both flasks are then processed as described below.

Cellulose powder — Construct an absorption tube from 150 mm glass tubing, 16 mm diameter, to one end of which is joined 50 mm tubing, 7 mm diameter. Push a small plug of cotton wool down the wide end of the absorption tube, then add 0.5 g cellulose powder (Whatman standard grade for chromatography) and tap the tube until the powder settles evenly. Insert another small cotton wool plug with light pressure to keep the powder in position. Connect the tube to the source of suction and collect the appropriate air sample.

Cellulose powder with zinc — Prepare an absorption tube as described above charged with an intimate mixture of 0.5 g cellulose powder and 0.1 g zinc metal dust. Collect the air sample as before.

Reduction in the nitro-group

Whatman filter paper — To the flask containing the filter papers add 10 ml of a mixture of equal volumes of ethanol and *N* HCl. Add approximately 0.1 g zinc dust. Add 1 drop of copper sulphate solution and swirl the flask for 2 to 5 minutes. Filter the liquid through a small cotton wool plug placed in the cone of a small glass funnel and previously washed with a little of the acid ethanol. Collect the filtrate in a tube graduated at 20 ml; wash the remaining contents of the flask with 5 ml acid ethanol and pour this through the funnel.

Cellulose powder — Clamp the absorption tube vertically and add a mixture of equal volumes of *N* HCl and ethanol. Collect 10 ml of the effluent solution in a tube or cylinder provided with a glass stopper and calibrated at 10 ml. Add about 0.1 g zinc dust and 1 drop copper sulphate solution, shake for 2 to 5 minutes, filter through cotton wool into a stoppered tube graduated at 20 ml as above and wash through with 5 ml acid ethanol.

Cellulose powder with zinc — In this procedure the reduction takes place in the cellulose column and subsequent filtration is not necessary. Wash the column through with acid ethanol to which has been added 1 drop copper sulphate solution for every 10 ml, and collect 10 ml of the effluent solution as above, in a stoppered tube bearing calibrations at 10 and 15 ml.

Production of azo-colour

To the solution of reduced parathion add 1 ml sodium nitrite solution, mix and leave for 15 minutes. Add 1 ml sulphatoethyl-*m*-toluidine solution and immediately afterwards 2.5 ml 3*M* sodium acetate solution, mix and leave for 10 minutes. Add 6 drops concentrated hydrochloric acid, which should be sufficient to convert the azo dye from yellow to bright red, and adjust the volume to 20 ml with distilled water. This is the procedure for the 15 ml solution from the filter paper and cellulose powder sampling procedure; the 10 ml solution from the procedure in which reduction takes place in the column requires only 2 ml sodium acetate solution and the final volume is adjusted to 15 ml.

Measurement of colour

The optical density of the coloured solution is measured at 510 mμ, selected by means of a monochromator or suitable filter, and then applied to a standard curve constructed from a series of parathion solutions subjected to the same reduction and colour development procedure. Alternatively, the test solution may be compared visually with a set of standard colour solutions prepared in a similar manner. The parathion content of the atmosphere is derived from a consideration of the the volume and parathion content of the air sample. In all measurements of atmospheric concentrations a blank experiment should be performed by subjecting the air filter medium to the same analytical treatment; the apparent parathion content obtained in this procedure should be subtracted from the parathion content of the air sample before the atmospheric concentration is calculated.

RESULTS

Recovery experiments

The efficiency of the recovery of parathion collected by the filtration medium from the air sample was tested by adding, by means of a micrometer syringe, 0.05 ml 40 mg % parathion in ethanol to filter paper or to the top of the cellulose columns. This corresponded to the addition of 20 μg parathion. After the solvent had evaporated, the procedures described above were completed. The optical densities were measured by means of a Unicam SP 350 spectrophotometer, using 1 in. cylindrical cells. The results obtained were applied to a standard curve prepared by treating 10 ml of a series of solutions containing up to 60 μg parathion in a similar manner. The standard curve for the cellulose-zinc column was prepared from solutions containing a range of amounts of parathion in 8 ml acid ethanol, the cotton wool filter being washed with sufficient acid ethanol to bring the volume to 10 ml followed by the procedure described in the previous section; the final volume was adjusted to 15 ml. The results obtained in these recovery experiments are shown in Table I.

TABLE I

RECOVERY OF 20 μg PARATHION FROM FILTRATION MEDIUM

Air sampling method	*μg Parathion found*	*% Recovery*
Filter paper	20	100
Cellulose powder	18.6	93
Cellulose powder with zinc	20	100

Analysis of test atmospheres

A test atmosphere, designed to contain 0.1 mg/m^3 parathion, was generated by the controlled atomisation of a solution of parathion in a metered stream of air, using the apparatus previously described[6]. The volume of air sampled was 200 l at a rate of 5 l per min. By the three sampling methods described, the recovery of parathion was between 80 and 100% of the expected value. With an expected concentration of 0.25 mg/m^3 parathion the filter paper method gave a 50% recovery.

DISCUSSION

The excellent recoveries of a known amount of parathion added to the filtration medium used to separate parathion from the air sample indicates that the analytical procedure is reliable and capable of faithfully recording the amount collected from the atmosphere. The poor recovery from the atmosphere expected to contain 0.25 mg/m^3 is not a criticism of the method of analysis, but of the atmosphere; either this concentration was in excess of the saturated vapour concentration of parathion or the atomised droplets were not evaporating sufficiently rapidly and the particulate parathion was being deposited on the walls of the mixing chamber before it reached the sampling orifice. There may be a similar cause for the slightly low recoveries at 0.1 mg/m^3, although the figures obtained can be regarded as quite satisfactory.

The third paper used in the filter paper method of separation of parathion from the air sample is present to ensure that the other two papers are efficiently performing their task. In all of the experiments made in the present investigation the parathion collected on this guard paper was negligible. An amount found on this paper less than 10% of that on the other two may be added to give the total collected; if more than 10% is found, then there is an indication that the first two papers contain faults or perforations and the experiment should be repeated.

With the spectrophotometer used in the present investigation the amount of parathion which can be measured with accuracy is 10 to 60 μg. If an amount in excess of this is present the coloured solution may be diluted with water and the optical density read again, or more accurately, the test should be repeated with a smaller air sample.

The blank experiment carried out in conjunction with each test should be only a faint pink in colour, equivalent to not more than 5 μg parathion. If a high blank is obtained the most likely source is the ethanol, which should then be purified by redistillation.

In this laboratory sulphatoethyl-*m*-toluidine is preferred as a coupling component to the more generally recommended naphthylethylenediamine. It has been our experience that samples of the latter commercially available are of very variable purity and may give high blank values in the test. Moreover, this reagent, and the ammonium sulphamate solution which is necessary to remove excess nitrite are both unstable and must be prepared at frequent intervals. If it is desired to use this reagent in the method described above, add to the solution after diazotisation with sodium nitrite, 1 ml 2.5% ammonium sulphamate solution, followed after 10 min. by 1 ml 1% *N*-(1-naphthyl)-ethylenediamine dihydrochloride solution, and the optical density is read 10 min later at 555 mμ.

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SUMMARY

A sensitive method is described for the determination of parathion in air. The air sample is drawn through filter paper or cellulose powder, which traps both particles and vapour, and the parathion is reduced without heating by means of a zinc-copper couple in acid solution, followed by diazotisation of the amino derivative and coupling to give an azo dye. An alternative procedure is described in which the parathion is trapped on cellulose powder containing zinc dust, from which the reduced derivative is directly eluted.

RÉSUMÉ

Une méthode sensible est décrite pour le dosage du ,,parathion'' dans l'air. L'échantillon d'air à analyser est passé à travers un papier filtre, ou à travers de la poudre de cellulose, qui retient les particules et la vapeur; le ,,parathion'' est réduit, sans chauffage, au moyen du couple zinc-cuivre, en solution acide; on effectue ensuite une diazotation du dérivé aminé et une copulation pour obtenir un colorant azoïque. Un autre procédé est décrit dans lequel le ,,parathion'' est absorbé sur de la poudre de cellulose, renfermant du zinc en poudre, à partir de laquelle le composé réduit est directement élué.

ZUSAMMENFASSUNG

Eine empfindliche Methode zur Bestimmung von Parathion in der Luft wird beschrieben. Die Luftprobe wird durch Filtrierpapier oder Zellulosepulver geleitet, welches sowohl Teilchen wie Dampf auffängt, und das Parathion wird ohne Erhitzen mit Hilfe von Kupfer-Zink in saurer Lösung reduziert, gefolgt von Diazotierung des Aminoderivates und Kupplung zu einem Azofarbstoff. Ein zweites Verfahren wird beschrieben, in welchem das Parathion in zinkstaubhältigem Zellulosepulver aufgefangen wird, aus welchem das reduzierte Derivat direkt eluiert wird.

REFERENCES

[1] R. C. HIRT AND J. B. GISCLARD, *Anal. Chem.*, 23 (1951) 185.
[2] N. STRAFFORD, C. R. N. STROUTS AND W. V. STUBBINGS, *The Determination of Toxic Substances in Air*, Heffer, Cambridge, 1956.
[3] P. R. AVERELL AND M. V. NORRIS, *Anal. Chem.*, 20 (1948) 753.
[4] J. C. GAGE, *Analyst*, 75 (1950) 189.
[5] R. FRAZIER, *Ind. Hyg. Newsletter, U.S. Public Health Service*, 10 (1950) 4.
[6] W. M. DIGGLE AND J. C. GAGE, *Analyst*, 78 (1953) 473.

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THERMOLYSIS OF THORIUM PRECIPITATES

II. SALTS OF ORGANIC ACIDS

by

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This is the second in a series of papers on the investigation of the thermal decomposition of the precipitates of thorium with organic acids[1]. Information of this type is needed because a number of the salts are of a basic nature and may often be of a variable composition. Consequently, the precipitated compounds are ignited and weighed as thorium oxide. The exact temperature limits for the ignition are frequently not given in the literature. As in the first paper of this series, the precipitated salts were sometimes of such a composition that they could be weighed directly, a fact which the original investigators failed to discover.

The thorium salts of the organic acids studied in this investigation have previously been prepared. They are the thorium salts of anisic acid (*p*-methoxybenzoic acid)[2], succinic acid[3], *o*-chlorobenzoic acid[4], adipic acid[3], *dl*-camphoric acid[5], *m*-iodobenzoic acid[6], *α*-naphthaleneacetic acid[7], *o*-toluic acid (*o*-methylbenzoic acid)[8], vanillic acid (4-hydroxy-3-methoxybenzoic acid)[9], and *p*-aminobenzoic[10].

EXPERIMENTAL

Reagents. Thorium nitrate tetrahydrate was obtained from the Lindsay Chemical Co., West Chicago, Ill.

The organic acids were obtained from Eastman Organic Chemicals, Rochester 3, New York; Aldrich Chemical Co., Milwaukee 12, Wisconsin; and Eastern Chemical Corp., Newark 2, New Jersey.

All other reagents were of C. P. quality.

Thermobalance. The thermobalance used has been previously described[11]. The sample weights and heating rates were the same as in the previous paper[1].

Preparation of the precipitates. The thorium salts of the organic acids were prepared as previously described[2-10]. The general procedure is reviewed in the previous paper[1]. In all cases, the precipitated salts were air dried at room temperature for at least 24 hours before pyrolysis on the thermobalance.

DISCUSSION

The thermal decomposition curves are shown in Figs. 1 and 2. In general, the precipitated salts exhibited varying degrees of stability. The first weight losses occurred from 50° to 310°C. The salts of basic composition were generally the least stable, while the normal salts exhibited the greatest stability. After various stages of decomposition, the oxide levels were obtained in the temperature range of 385° to 600°C. The oxide levels were reached in all cases far below the 1000°C ignition temperature advocated by some of the investigators. The minimum oxide level temperatures are listed in Table I.

TABLE I

MINIMUM OXIDE LEVEL TEMPERATURES FOR THE THORIUM SALTS OF ORGANIC ACIDS

	Precipitate	*Temperature °C*[a]
1.	Thorium anisate	475
2.	Thorium succinate	600
3.	Thorium *o*-chlorobenzoate	505
4.	Thorium adipate	450
5.	Thorium camphorate	475
6.	Thorium *m*-iodobenzoate	540
7.	Thorium *α*-naphthaleneacetate	530
8.	Thorium *o*-toluate	440
9.	Thorium vanillate	385
10.	Thorium *p*-aminobenzoate	465

[a] Heating rate of 4.5°C per minute.

Thorium succinate. The thermal decomposition curve of thorium succinate is shown in Fig. 1. The precipitated compound corresponded to the formula for the basic salt, $Th(OH)_2[OOC(CH_2)_2COOH]_2$, although it was probably contaminated with $Th(OH)_4$. The precipitated salt was stable up to 55°C where it began to lose weight, resulting in a nearly horizontal level from 215° to 345°C. The organic matter was oxidized beyond 345°C, giving the ThO_2 level at 600°C. This salt has mainly been used to separate thorium from the cerite rare earth group[3].

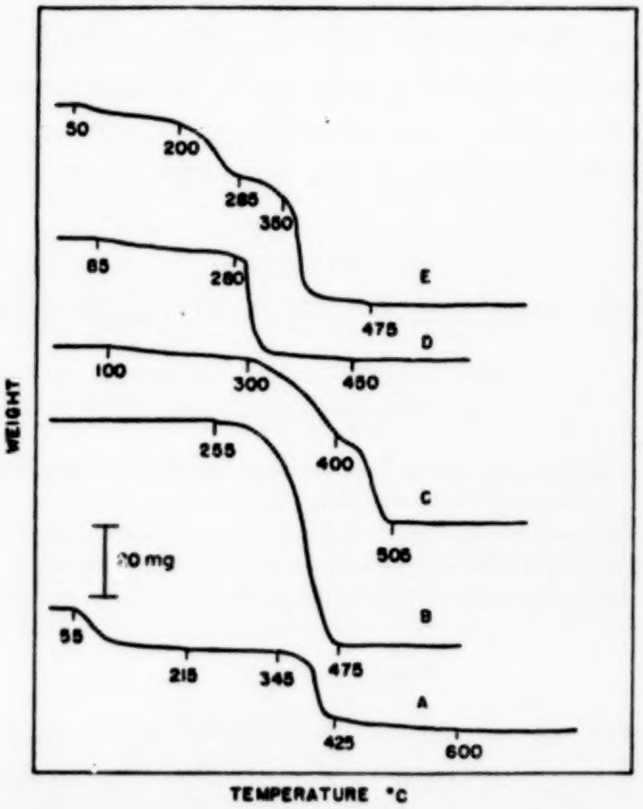

Fig. 1. Thermal decomposition curves of thorium salts of organic acids
Curve A. Thorium succinate
Curve B. Thorium anisate
Curve C. Thorium *o*-chlorobenzoate
Curve D. Thorium adipate
Curve E. Thorium camphorate

Thorium anisate. The thermal decomposition curve of thorium anisate is shown in Fig. 1. The precipitated compound corresponded to the formula for the normal salt, $Th(CH_3OC_6H_4COO)_4$, in agreement with previous investigators[2].

The precipitate was stable up to 255°C, beyond which it rapidly decomposed to give the ThO_2 level at 475°C.

This salt has been useful in the separation of thorium from uranium[2].

Thorium o-*chlorobenzoate.* The thermal decomposition curve of thorium *o*-chlorobenzoate is shown in Fig. 1. The precipitated compound corresponded to the formula for the basic salt, $Th(OH)_2(ClC_6H_4COO)_2$. Previous investigators assigned the formula $Th(OH)(ClC_6H_4COO)_3 \cdot 3H_2O$ to the salt[4]. The precipitate was stable up to 100°C where it began to lose weight slowly. At 300°C, the rate of weight loss increased giving a short inflection in the curve at 400°C and then the ThO_2 level at 505°C. It is stated that this salt or the *m*-nitrobenzoic acid salt gave satisfactory recovery of thorium in the presence of 50 to 60 times the amount of uranium[4].

Thorium adipate. The thermal decomposition curve of thorium adipate is shown in Fig. 1. The precipitated compound corresponded to the formula for the basic salt, $Th(OH)_3[OOC(CH_2)_4COOH]$. The basic salt was stable up to 85°C where it began to lose weight slowly. At 280°C, the organic matter began to oxidize giving the ThO_2 level at 450°C. Adipic acid is said to precipitate thorium quantitatively[3].

Thorium camphorate. The thermal decomposition of thorium camphorate is shown in Fig. 1. The precipitated compound corresponded to the formula for the normal salt, $Th[C_8H_{14}(COO)_2]_2$, in agreement with that of other investigators[5]. The precipitate was stable up to 50°C where it began to lose weight slowly. At 200°C, the rate of decomposition increased, giving a break in the curve at 285°C. Beyond 350°C, the remaining organic matter was oxidized giving the ThO_2 level at 475°C. Previous investigators recommended drying the precipitate at 105°C or ignition to ThO_2, the latter method being preferred. As can be seen from the curve, a level was not obtained at 105°C so that these results confirm the suggestion that the precipitate should be ignited to the oxide.

Thorium p-*aminobenzoate.* The thermal decomposition curve for thorium *p*-aminobenzoate is shown in Fig. 2. The precipitated compound corresponded to the formula for the basic salt, $Th(OH)_3(NH_2C_6H_4COO)$. The formula proposed by the original investigators was $(O)Th(OH)(NH_2C_6H_4COO) \cdot 4H_2O$[10], which is approximately equivalent to the one found in this investigation. This salt differed from that of the *o*-aminobenzoic acid salt which had the formula $Th(OH)_2(NH_2C_6H_4COO)_2$[1].

The precipitated basic salt was stable up to 75°C, where it began to lose weight slowly. The remaining organic matter was oxidized beginning at 350°C, resulting in the formation of the ThO_2 level at 465°C. This organic acid enabled the separation of thorium from the rare earth elements if the pH was adjusted properly.

Thorium m-*iodobenzoate.* The thermal decomposition curve of thorium *m*-iodobenzoate is shown in Fig. 2. The formula for the precipitated compound corresponded to the normal salt, $Th(IC_6H_4COO)_4$, in contrast to the formula proposed by the original investigators of $Th(OH)_2(IC_6H_4COO)_2$[6]. This salt was perhaps one of the most stable of all the compounds studied, the first weight loss occurred beyond 300°C. Above this temperature, the organic matter was oxidized rapidly resulting in the ThO_2 level at 540°C.

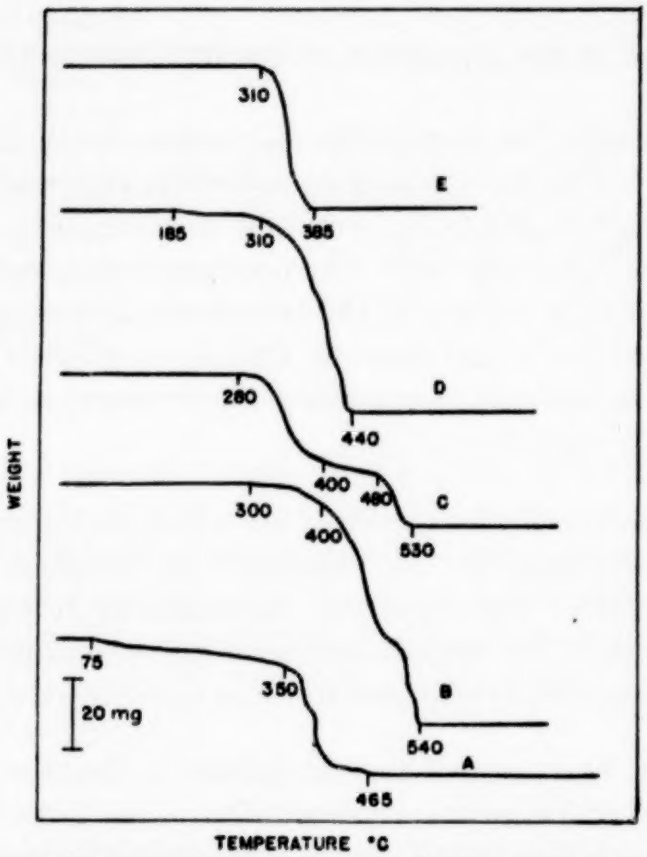

Fig. 2. Thermal decomposition curves of thorium salts of organic acids
Curve A. Thorium *p*-aminobenzoate
Curve B. Thorium *m*-iodobenzoate
Curve C. Thorium *α*-naphthaleneacetate
Curve D. Thorium *o*-toluate
Curve E. Thorium vanillate

Thorium α-naphthaleneacetate. The thermal decomposition curve of thorium *α*-naphthaleneacetate is shown in Fig. 2. The precipitated compound corresponded to the formula for the normal salt, $Th(C_{10}H_7CH_2COO)_4$. Previous investigators assigned the formula $Th(OH)_3(C_{10}H_7CH_2COO)$, after washing the precipitated compound with hot 90% ethyl alcohol and drying at 105 to 110°C[7].

The salt was quite stable, the first weight loss occurred above 280°C. Beyond this temperature, the salt decomposed rapidly giving a break in the curve at 400°C. At 480°C, the remaining organic matter was oxidized resulting in the ThO_2 level at 530°C.

This organic acid shows definite promise as a precipitating agent for thorium. The precipitated salt had been previously ignited to the oxide but from the thermal decomposition curve, it is seen that it may be possible to weigh the precipitate directly.

Thorium o-toluate. The thermal decomposition curve of thorium *o*-toluate is shown in Fig. 2. The formula for the precipitated compound corresponded to $Th(CH_3C_6H_4COO)_4$. The salt was stable up to 185°C where there was a small loss in weight. Beyond 310°C, the organic matter was oxidized rapidly resulting in the ThO_2 level at 440°C. The original investigators claimed that this organic acid gave results which agreed quite well with the well known *m*-nitrobenzoic acid procedure[8].

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Thorium vanillate. The thermal decomposition curve of thorium vanillate is shown in Fig. 2. The precipitated compound corresponded to the formula for the normal salt, $Th[CH_3O(OH)C_6H_3COO]_4$. Previous investigators reported a basic salt whose formula was said to be $Th(OH)[CH_3O(OH)C_6H_3COO]_3 \cdot 2H_2O$[9]. This salt was the most stable of all the thorium salts studied. The first weight loss occurred at 310°C, beyond which the organic matter was oxidized quite rapidly to give the ThO_2 level at 385°C.

The original investigators ruled out the possibility of weighing the precipitated salt directly and ignited it to the oxide[9]. They stated that thorium was quantitatively precipitated from solution by the use of this acid. From the thermal decomposition curve it can be seen that perhaps the precipitated salt could the weighed directly.

SUMMARY

The thermal decomposition of the thorium salts of anisic, succinic, *o*-chlorobenzoic, adipic, *dl*-camphoric, *m*-iodobenzoic, *α*-naphthaleneacetic, *o*-toluic, vanillic and *p*-aminobenzoic acids were investigated on the thermobalance. The first weight losses occurred in the temperature range of 50° to 310°C. After various stages of decomposition, the oxide levels were obtained from 385° to 600°C.

RÉSUMÉ

La décomposition thermique des sels de thorium des acides anisique, succinique, *o*-chlorobenzoique, adipique, *dl*-camphorique, *m*-iodobenzoïque, *α*-naphtalinacétique, *o*-toluique, vanillique et *p*-aminobenzoïque a été examinée sur la thermobalance. Les premières pertes de poids se produisent entre 50 et 310°C. Après plusieurs stades de décomposition, les paliers des oxydes ont été obtenus de 385 à 600°C.

ZUSAMMENFASSUNG

Die thermische Zersetzung der Thoriumsalze von Anisinsäure, Bernsteinsäure, *o*-Chlorbenzoësäure, Adipinsäure, *dl*-Kampfersäure, *m*-Jodbenzoësäure, *α*-Naphtalinessigsäure, *o*-Toluylsäure, Vanillinsäure und *p*-Aminobenzoësäure wurden auf der Thermowaage untersucht. Die ersten Gewichtsverluste wurden in dem Temperaturbereiche von 50 bis 310°C beobachtet. Nach verschiedenen Zersetzungsstadien wurden die Oxydstufen zwischen 385 und 600°C erreicht.

REFERENCES

[1] W. W. WENDLANDT, *Anal. Chem.*, 29 (1957) 800.
[2] K. V. S. KRISHNAMURTY AND BH. S. V. RAGHAVA RAO, *J. Indian Chem. Soc.*, 28 (1951) 261; *Rec. trav. chim.*, 70 (1951) 421.
[3] T. V. S. SURYANARAYANA AND BH. S. V. RAGHAVA RAO, *J. Indian Chem. Soc.*, 28 (1951) 511.
[4] B. R. LAKSHMANA AND BH. S. V. RAGHAVA RAO, *J. Indian Chem. Soc.*, 27 (1950) 457, 610.
[5] D. S. N. MURTY AND S. V. RAGHAVA RAO, *J. Indian Chem. Soc.*, 28 (1951) 218.
[6] S. K. DATTA AND G. BANERJEE, *J. Indian Chen. Soc.*, 32 (1955) 167.
[7] S. K. DATTA AND G. BANERJEE, *Anal. Chim. Acta*, 12 (1955) 38.
[8] B. R. LAKSHMANA AND BH. S. V. RAGHAVA RAO, *J. Indian Chem. Soc.*, 27 (1950) 569.
[9] K. V. S. KRISHNAMURTY AND A. PURUSHOTTAM, *Rec. trav. chim.*, 71 (1952) 671.
[10] D. S. N. MURTY AND BH. S. V. RAGHAVA RAO, *J. Indian Chem. Soc.*, 27 (1950) 459.
[11] W. W. WENDLANDT, *Anal. Chem.*, 27 (1955) 1277.

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RÉDUCTION ÉLECTROCHIMIQUE DE L'EAU ET DE SES IONS

II. CAS DES ACIDES FAIBLES ET DES MÉLANGES TAMPONS

par

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Dans un précédent mémoire, nous avons étudié les courbes de polarisation de l'eau et de ses ions en présence d'une électrode de platine platiné[1]. Les solutions considérées alors contenaient uniquement un acide fort ou une base forte donc des ions H^+ ou OH^- et le système oxydo-réducteur H(O)/H(I) ne faisait intervenir que les ions de l'eau. Nous nous sommes proposé d'examiner le comportement du système H(O)/H(I) en présence de platine platiné, lorsque les solutions contiennent différents acides faibles ou mélanges tampons.

PARTIE THÉORIQUE

Précédemment[1], nous avons étudié la réduction de H^+ et celle de H_2O en considérant H_2O comme un complexe hydroxylé de H^+: nous avons vérifié que suivant la nature des ions en solution et le potentiel considéré, deux réactions électrochimiques distinctes sont possibles, à savoir:

Réduction des ions hydrogène: $2\,H^+ + 2\,e \rightleftarrows H_2$ . . . . (1)

Réduction de l'eau: $2\,H_2O + 2\,e \rightleftarrows H_2 + 2\,OH^-$ . . . . (2)

soit (1) réduction de H^+ libre, (2) réduction de H^+ complexé par OH^-.

Nous avons généralisé ces résultats en étudiant la réduction d'acides faibles, c'est-à-dire de H^+ complexé par différentes bases ($CH_3CO_2^-$, $HPO_4^{=}$, C_5H_5N, BO_2^-).

Dans tout ce qui suit, nous supposons comme le justifient nos résultats expérimentaux, que:

toutes les réactions électrochimiques en présence de platine platiné sont rapides,

les différentes bases complexant H^+ ne sont pas électroactives,

les vitesses de dissociation et de recombinaison des différents couples acides-bases sont suffisamment grandes devant les vitesses de réaction à l'électrode pour ne pas intervenir dans la cinétique du processus électrochimique,

la réaction globale d'oxydo-réduction peut s'écrire:

$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$ . . . . (3)

Nous allons établir l'équation de la courbe de polarisation correspondant à la réaction (3) en supposant négligeable le phénomène de migration des ions électroactifs. Cette

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condition est réalisée expérimentalement en utilisant un électrolyte indifférent suffisamment concentré. L'intensité du courant est alors limitée par la diffusion des espèces réagissant à l'électrode[2,3].

Si la concentration des ions H^+ libres en solution est suffisamment faible pour que le courant d'électrolyse dû à leur réduction directe (I) soit négligeable au potentiel considéré, nous pouvons considérer uniquement la réaction (3):

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

En supposant: cette réaction électrochimique rapide, les concentrations égales aux activités, le potentiel d'électrode est donné par la loi de Nernst.

$$E = E_\circ' + \frac{0.059}{2} \log \frac{[HA]_e^2}{[A^-]_e^2\,[H_2]_e}$$

Dans cette équation, $E_\circ'$ est le potentiel normal d'équilibre de la réaction (3), $[HA]_e$, $[A^-]_e$ et $[H_2]_e$ les concentrations de l'acide HA, de la base A^- et de l'hydrogène dissous au voisinage de l'électrode.

D'autre part:

$$\begin{aligned} i &= k_{HA}\,([HA]_e - [HA]_s) \\ i &= k_{A^-}([A^-]_s - [A^-]_e) \\ i &= k_{H_2}([H_2]_s - [H_2]_e) \\ i_{HA} &= -k_{HA}[HA]_s \\ i_{A^-} &= k_{A^-}\,[A^-]_s \\ i_{H_2} &= k_{H_2}\,[H_2]_s \end{aligned}$$

Dans ces équations, i représente l'intensité du courant, négative pour un courant de réduction (cathodique), positive pour un courant d'oxydation (anodique), i_{HA}, i_{A^-} et i_{H_2} les intensités des courants de diffusion, k_{HA}, k_{A^-} et k_{H_2} les coefficients de diffusion, $[HA]_s$, $[A^-]_s$ et $[H_2]_s$ les concentrations au sein de la solution de l'acide HA, de la base A^- et de l'hydrogène dissous.

Donc:

$$E = E_\circ' + \frac{0.059}{2} \log \frac{k_{H_2}(k_{A^-})^2}{(k_{HA})^2} + \frac{0.059}{2} \log \frac{(i - i_{AH})^2}{(i_{A^-} - i)^2(i_{H_2} - i)}$$

$E_\circ'$ n'est pas indépendant de $E_\circ$ potentiel normal d'équilibre du système:

$$2\,H^+ + 2\,e \rightleftarrows H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

En effet, puisque nous admettons que les vitesses de recombinaison et de dissociation du couple acide-base sont grandes devant les vitesses de réaction électrochimique, les ions présents à l'électrode sont en équilibre chimique soit:

$$\frac{[H^+]_e\;[A^-]_e}{[HA]_e} = K_A$$

K_A désignant la constante d'acidité du couple HA/A^-.

Le potentiel d'électrode est donné par les relations:

$$E = E_\circ + \frac{0.059}{2} \log \frac{[H^+]_e^2}{[H_2]_e} \qquad = E_\circ' + \frac{0.059}{2} \log \frac{[HA]_e^2}{[H_2]_e\,[A^-]_e^2}$$

d'où:

$$E_\circ{}' = E_\circ - 0.059\ \mathrm{p}K_\mathrm{A}$$

Donc:

$$E = E_\circ - 0.059\ \mathrm{p}K_\mathrm{A} + \frac{0.059}{2} \log \frac{k_{\mathrm{H_2}}(k_{\mathrm{A^-}})^2}{(k_{\mathrm{HA}})^2} + \frac{0.059}{2} \log \frac{(i - i_{\mathrm{HA}})^2}{(i_{\mathrm{A^-}} - i)^2\,(i_{\mathrm{H_2}} - i)} \quad \ldots\ldots \quad (3)$$

Dans le cas particulier où le couple HA/A^- n'est autre que HOH/OH^-, nous avions obtenu l'équation suivante de la courbe de polarisation[1]:

$$E = E_\circ - 0.059\ \mathrm{p}K_{\mathrm{H_2O}} + \frac{0.059}{2} \log k_{\mathrm{H_2}}(k_{\mathrm{OH^-}})^2 - \frac{0.059}{2} \log (i_{\mathrm{OH^-}} - i)^2\,(i_{\mathrm{H_2}} - i) \quad \ldots \quad (2')$$

A la réduction des ions hydrogène non complexés suivant la réaction

$$2\,H^+ + 2\,e \rightleftarrows H_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

correspond une courbe de polarisation d'équation:

$$E = E_\circ + \frac{0.059}{2} \log \frac{k_{\mathrm{H_2}}}{(k_{\mathrm{H^+}})^2} + \frac{0.059}{2} \log \frac{(i - i_{\mathrm{H^+}})^2}{(i_{\mathrm{H_2}} - i)} \quad \ldots\ldots\ldots\ldots \quad (1')$$

Remarque

Nous pourrions conduire les calculs d'une façon différente en décomposant la réaction d'oxydo-réduction en une réaction électrochimique (a):

$$2\,H^+ + 2\,e \rightleftarrows H_2$$

et une réaction chimique infiniment rapide (b):

$$H^+ + A^- \rightleftarrows HA$$

Le potentiel d'électrode est déterminé par les concentrations à l'électrode de H^+ et de H_2, soit:

$$E = E_\circ + \frac{0.059}{2} \log \frac{[H^+]_e^2}{[H_2]_e}$$

Mais si l'équilibre chimique est réalisé instantanément à l'électrode:

$$\frac{[H^+]_e\,[A^-]_e}{[HA]_e} = K_\mathrm{A}$$

donc:

$$E = E_\circ - 0.059\ \mathrm{p}K_\mathrm{A} + \frac{0.059}{2} \log \frac{[HA]_e^2}{[H_2]_e\,[A^-]_e}$$

Nous retrouvons la formule de départ de la première méthode de calcul.

PARTIE EXPÉRIMENTALE

Nous avons utilisé le même type de cellule d'électrolyse et le même type d'électrode indicatrice que précédemment[1].

Ayant eu quelques difficultés à tracer les courbes de polarisation anodique à cause de l'instabilité du courant et du potentiel, nous avons intercalé dans le montage précédemment décrit un potentiostat Telec qui, en maintenant constant le potentiel de l'électrode indicatrice, stabilise également l'intensité du courant.

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Résultats expérimentaux

Nous avons successivement considéré les cas suivants:

1. Mélanges tampons $[A^-]_s \neq [HA]_s$ de nature et de concentration variables, en présence ou non d'hydrogène.

2. Acide faible de concentration variable en présence ou non d'ions H^+ libres.

3. Acide très faible de concentration constante en présence de la base correspondante de concentration variable.

1. Cas des mélanges tampons

1.1. En l'absence d'hydrogène (Fig. 1)

La courbe de polarisation cathodique d'une solution neutre non tamponnée (chlorure de sodium M) est figurée ici en traits mixtes. Nous avons précédemment[1] vérifié que sa position et sa forme correspondaient à la réduction directe de l'eau suivant la réaction:

$$2\,H_2O + 2\,e \rightleftarrows H_2 + 2\,OH^-$$

la quantité d'ions H^+ libres en solution étant insuffisante pour que leur réduction donne lieu à un courant notable.

La Fig. 1 reproduit les courbes de polarisation cathodique de différentes mélanges tampons. La réduction de chacun d'eux a lieu suivant la réaction:

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

car les couples acides-bases étudiés ont tous un pK suffisamment grand pour que la réduction des ions H^+ libres soit négligeable.

D'après les calculs développés plus haut, ces courbes ont une équation de la forme:

$$E = A + \frac{0.059}{2} \log \frac{(i - i_{HA})^2}{(i_{A^-} - i)^2\,(-i)}$$

a) Lorsque la solution est suffisamment concentrée en mélange tampon, i est négligeable à la fois devant i_{A^-} et i_{HA} et:

$$E = A + 0.059 \log \left[\frac{-i_{HA}}{i_{A^-}}\right] - \frac{0.059}{2} \log(-i)$$

Nous avons étudié expérimentalement la fonction $E = f[\log(-i)]$ pour différents mélanges tampons. Les courbes obtenues sont des droites de coefficient angulaire:

—32 mV/unité de log pour un tampon acétique 0.1 M,
—32 mV/unité de log pour un tampon phosphorique 0.1 M,
—34 mV/unité de log pour un tampon borique 0.1 M.
(valeur théorique à la température ordinaire: —30 mV/unité de log).

b) Lorsque la concentration de la solution en mélange tampon diminue et que i et i_{HA} deviennent du même ordre de grandeur, il est possible de mettre en évidence la réduction successive des ions H^+ complexés par A^- (réduction de HA) et des ions H^+ complexés par OH^- (réduction de H_2O). Ainsi, la courbe 5 de la Fig. 1 (tampon acétique 0.001 M) présente un palier dont la hauteur est proportionnelle à la concentration du tampon en solution et une partie verticale qui se confond avec la courbe obtenue en milieu neutre: cette partie correspond à la réduction directe de l'eau.

1.2. En présence d'hydrogène (Fig. 2)

En milieu non tamponné (courbe 5 de la Fig. 2), nous avons précédemment démontré que: la réduction de l'eau a lieu suivant la réaction:

$$2\,H_2O + 2\,e \rightleftarrows H_2 + 2\,OH^-$$

sans limitation de l'intensité cathodique;
l'oxydation de l'hydrogène a lieu suivant la réaction:

$$H_2 \rightleftarrows 2\,H^+ + 2\,e$$

avec limitation de l'intensité anodique par la diffusion de l'hydrogène dissous.

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Nous avons étudié les courbes de polarisation anodique et cathodique de différentes solutions de tampon phosphorique. La réaction oxydo-réductrice est alors:

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

D'après les calculs développés plus haut, l'équation de ces courbes est de la forme:

$$E = A + \frac{0.059}{2} \log \frac{(i - i_{HA})^2}{(i_{A^-} - i)^2\,(i_{H_2} - i)}$$

L'intensité anodique peut être limitée soit par la diffusion de H_2, soit par celle de A^- si la solution est suffisamment peu concentrée en A^-. L'intensité cathodique est éventuellement limitée par la diffusion de HA.

a) Lorsque la solution est suffisamment concentrée en mélange tampon pour que i soit négligeable à la fois devant i_{HA} et i_{A^-}:

$$E = A + 0.059 \log \left|\frac{-i_{HA}}{i_{A^-}}\right| - \frac{0.059}{2} \log (i_{H_2} - i)$$

Nous avons étudié la fonction $E = f[\log(i_{H_2} - i)]$ pour une solution de tampon phosphorique $0.1\,M$. La courbe expérimentale obtenue est une droite de coefficient angulaire —32 mV/unité de log (valeur théorique: —30 mV/unité de log).

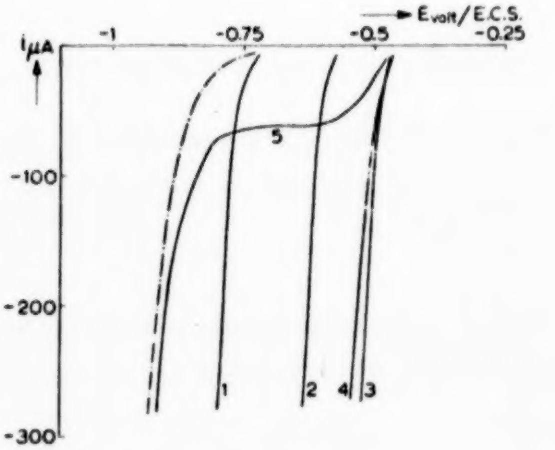

Fig. 1. Courbes de polarisation cathodique. En traits mixtes solution NaCl M;
Courbe 1. Tampon borique $0.1\,M$, NaClM; pH 9;
Courbe 2. Tampon phosphorique $0.1\,M$, NaCl M; pH 6.2;
Courbe 3: Tampon acétique $0.1\,M$; NaClM; pH 4.5;
Courbe 4: Tampon acétique $0.01\,M$; NaClM; pH 4.5;
Courbe 5: Tampon acétique $0.001\,M$; NaClM; pH 4.5.
Atmosphère d'azote. Électrode de platine platiné.

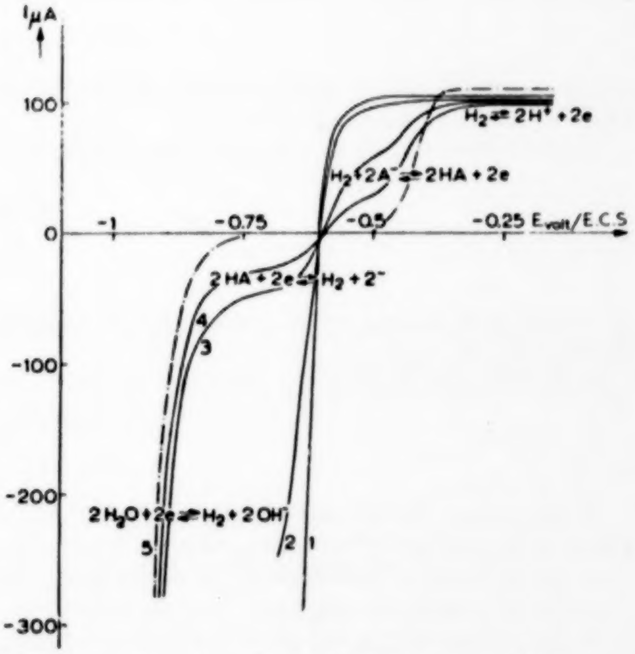

Fig. 2. Courbes de polarisation anodique et cathodique.
Courbe 1: Tampon phosphorique $0.1\,M$, NaCl M; pH 6.2;
Courbe 2: Tampon phosphorique $0.01\,M$, NaCl M; pH 6.2;
Courbe 3: Tampon phosphorique $0.002\,M$, NaCl M; pH 6.1;
Courbe 4: Tampon phosphorique $0.001\,M$, NaCl M; pH 6;
Courbe 5: Solution NaCl M.
Atmosphère d'hydrogène. Électrode de platine platiné.

b) Si la solution tampon est suffisamment diluée, il est possible de mettre en évidence:

du côté cathodique, à la fois la réduction des ions H^+ complexés par A^- (réduction de HA) limitée par la diffusion de HA, et celle des ions H^+ complexés par OH^- (réduction de H_2O);

du côté anodique, à la fois l'oxydation de l'hydrogène dissous limitée par la diffusion de A^- (réaction (3)) et par la diffusion de H_2 (réaction(1)).

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Ainsi, les courbes 3 et 4 de la Fig. 2 (tampon phosphorique 0.001 et 0.002M) présentent:

du côté cathodique un palier dont la hauteur est proportionnelle à la concentration en solution de l'acide du tampon et une partie verticale qui se confond avec la courbe obtenue en milieu neutre: cette dernière partie correspond à la réduction de l'eau;

du côté anodique une première vague dont la hauteur est proportionnelle à la concentration en solution de la base du tampon et une seconde vague qui se confond avec la vague unique obtenue en milieu neutre et correspond à l'oxydation de H_2 en milieu non complexant.

Remarque

Lorsque la concentration du tampon en solution devient inférieure à 0.0002M, les intensités des courants de diffusion de HA et de A^- sont de l'ordre de grandeur du courant résiduel et la courbe de polarisation d'une telle solution devient identique à celle d'une solution neutre non tamponnée (courbe 5 de la Fig. 2). Le potentiel d'équilibre de l'électrode à hydrogène oscille sur 250 mV, il est mal défini et non reproductible. Comme nous l'avions dit précédemment[1], l'expérience confirme très bien le fait qu'il est incorrect d'utiliser l'électrode à hydrogène pour mesurer un pH en milieu insuffisamment tamponné.

2. *Cas d'un acide faible*

Nous avons tracé les courbes de polarisation en présence d'hydrogène de solutions de chlorhydrate de pyridinium 0.003 et 0.006M (Fig. 3). Le cation pyridinium est un acide faible ($pK = 5.2$), suffisamment faible pour que de telles solutions ne contiennent qu'une quantité négligeable d'ions H^+ libres (de 0.0001 à 0.0002M).

Dans ces conditions, la seule réaction oxydo-réductrice à considérer est la réaction (3):

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

et les courbes de polarisation correspondantes ont pour équation:

$$E = A + \frac{0.059}{2} \log \frac{(i - i_{HA})^2}{(-i)^2\,(i_{H_2} - i)}$$

Nous avons étudié la fonction $E = f\left[\log \frac{(i - i_{HA})^2}{(-i)^2\,(i_{H_2} - i)}\right]$. Les courbes expérimentales obtenues sont des droites de coefficient angulaire respectif 30 et 32 mV/unité de log (valeur théorique: 30 mV/unité de log).

Lorsque la solution contient à la fois un acide faible et des ions H^+ libres, la courbe de polarisation cathodique est la somme des courbes cathodiques d'une solution d'acide faible et d'une solution diluée d'acide fort; les ions H^+ libres et les ions H^+ complexés étant réduits indépendamment. Les courbes expérimentales (courbes 1, 3 et 4 de la Fig. 3) confirment cette hypothèse.

3. *Cas d'un acide faible en présence de la base correspondante*

Nous avons étudié les courbes de polarisation en présence d'hydrogène de solutions d'acide borique et de borate.

a) Lorsque la solution contient uniquement de l'acide borique, acide très faible, la quantité d'ions H^+ libres en solution est négligeable et la seule réaction d'oxydo-réduction à considérer est:

$$2\,HBO_2 + 2\,e \rightleftarrows H_2 + 2\,BO_2^-$$

La courbe de polarisation cathodique d'une solution d'acide borique a donc pour équation d'après les calculs développés plus haut:

$$E = A + \frac{0.059}{2} \log \frac{(i - i_{HBO_2})^2}{(-i)^2\,(i_{H_2} - i)}$$

Si la solution est suffisamment concentrée en HBO_2, i est négligeable devant i_{HBO_2} et:

$$E = A - \frac{0.059}{2} \log\,(-i)^2\,(i_{H_2} - i)$$

La courbe de réduction d'une solution concentrée de HBO_2 est donc parallèle à la courbe de réduction de l'eau. La distance entre les deux courbes (fonction de la stabilité relative des deux complexes d'H^+: HBO_2 et H_2O) est donnée par la formule ci-dessus obtenue par soustraction des équations (2) et (3) (voir partie théorique)

$$\Delta E = 0.059 \left\{ (pK_{H_2O} - pK_{HBO_2}) + \log\,[HBO_2]_s - \log \left[\frac{k_{OH^-}}{k_{BO_2}}\right] \right\}$$

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En estimant le rapport $k_{OH^-}/k_{BO_2^-}$ à 2 d'après les mesures expérimentales:

$$\Delta E = 0.210 \text{ volt à } 20°C$$

Expérimentalement, nous avons trouvé pour ΔE la valeur 0.215 volt.

L'oxydation de l'hydrogène en présence d'acide borique seul a lieu suivant la réaction:

$$H_2 \rightleftarrows 2\,H^+ + 2\,e$$

La courbe de polarisation anodique a donc pour équation:

$$E = B + \frac{0.059}{2} \log \frac{(i)^2}{(i_{H_2} - i)}$$

Nous avons vérifié expérimentalement les équations des courbes anodique et cathodique; pour la partie anodique la fonction $E = f\left[\log \frac{(i)^2}{(i_{H_2} - i)}\right]$ est linéaire (coefficient angulaire 32 mV/unité de log)

pour la partie cathodique la fonction $E = f\,[\log (-i)^2\,(i_{H_2} - i)]$ est également linéaire (coefficient angulaire —32 mV/unité de log).

b) Lorsque les solutions d'acide borique contiennent une petite quantité de borate (courbes 3 et 4 de la Fig. 4), il est possible de mettre en évidence deux réactions successives d'oxydation de l'hydrogène soit:

$$H_2 + 2\,BO_2^- \rightleftarrows 2\,HBO_2 + 2\,e$$

et

$$H_2 \rightleftarrows 2\,H^+ + 2\,e$$

La hauteur de la première vague est proportionnelle à la concentration de BO_2^- en solution et celle de la seconde à la concentration de l'hydrogène dissous.

c) Lorsque la concentration en BO_2^- croît, la courbe de polarisation anodique ne présente plus qu'une seule vague correspondant à la réaction (1) et de hauteur proportionnelle à la concentration en solution de l'hydrogène dissous (courbes 4 et 5 de la Fig. 4).

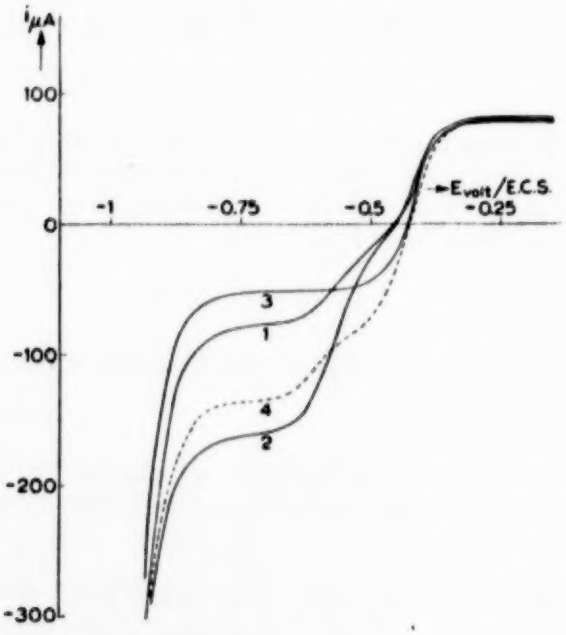

Fig. 3. Courbes de polarisation anodique et cathodique.
Courbe 1: Solution chlorhydrate de pyridinium 0.003*M*, NaCl *M*;
Courbe 2: Solution chlorhydrate de pyridinium 0.006*M*, NaCl *M*;
Courbe 3: Solution HCl env. 0.0007*M*, NaCl *M*;
Courbe 4: Solution chlorhydrate de pyridinium 0.003*M*, HCl env. 0.0007*M*, NaCl*M*.
Atmosphère d'hydrogène. Électrode de platine platiné.

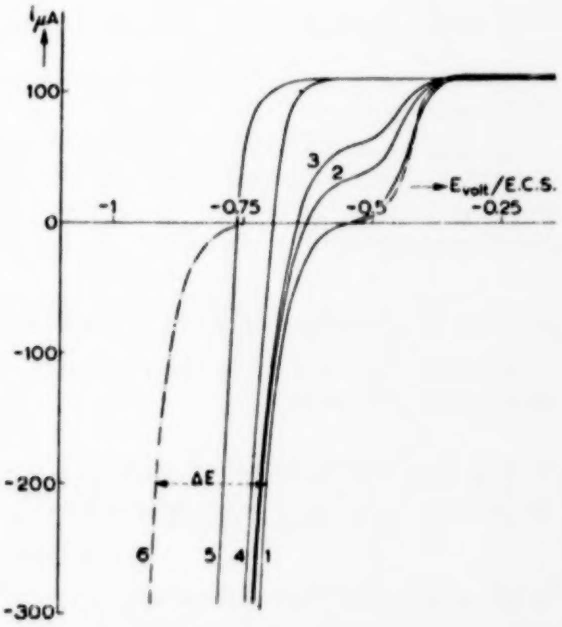

Fig. 4. Courbes de polarisation anodique et cathodique.
Courbe 1: Solution acide borique 0.1*M*, NaCl *M*;
Courbe 2: Solution acide borique 0.099*M*, borate de sodium 0.001*M*, NaCl *M*;
Courbe 3: Solution acide borique 0.098*M*, borate de sodium 0.002*M*, NaCl *M*;
Courbe 4: Solution acide borique 0.09*M*, borate de sodium 0.01*M*, NaCl *M*;
Courbe 5: Solution tampon borique 0.1*M*, NaCl *M*;
Courbe 6: Solution NaCl *M*.
Atmosphère d'hydrogène. Électrode de platine platiné.

Remarque

Lorsque la solution contient uniquement de l'acide borique, elle n'est pas tamponnée en ions H^+ et le potentiel de l'électrode à hydrogène est mal défini; par contre, dès que la solution d'acide borique contient une petite quantité de borate, elle est tamponnée en ions H^+: le potentiel de l'électrode à hydrogène est alors bien défini. Les courbes de polarisation de ces différentes solutions (Fig. 4) mettent en évidence les conditions d'utilisation correcte de l'électrode à hydrogène.

RÉSUMÉ

Nous avons vérifié que sur une électrode de platine platiné, les courbes de polarisation de solutions d'acides faibles ou de mélanges tampons peuvent s'interprêter en admettant l'existence d'une réaction électrochimique du type:

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

Cette réaction peut être considéré comme la somme de deux réactions distinctes, l'une électrochimique: réduction de H^+ libre, l'autre chimique: équilibre acide-base.

En supposant que: (1) le système oxydo-réducteur H_2/H^+ est rapide en présence de platine platiné, (2) les lois de l'équilibre chimique sont valables au voisinage de l'électrode, nous avons pu rendre compte des résultats expérimentaux obtenus.

SUMMARY

We have verified that, using a platinized platinum electrode, the polarization curves of solutions of weak acids or buffer mixtures can be interpreted, assuming the existence of an electrochemical reaction of the type:

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

This reaction can be considered as the sum of two distinct reactions, one electrochemical: reduction of free H^+, the other chemical: acid-base equilibrium.

Assuming that (1) the oxidation-reduction system H_2/H^+ is rapid in the presence of platinized platinum, and (2) the laws of chemical equilibrium hold in the vicinity of the electrode, we have been able to give an account of the experimental results obtained.

ZUSAMMENFASSUNG

Es wurde bewiesen, dass man auf einer platinierten Platinelektrode die Polarisationskurven von Lösungen schwacher Säuren oder von Puffergemischen interpretieren kann, indem man die Existenz einer elektrochemischen Reaktion der folgenden Art annimmt:

$$2\,HA + 2\,e \rightleftarrows H_2 + 2\,A^-$$

Diese Reaktion kann als die Summe zweier verschiedener Reaktionen aufgefasst werden: eine elektrochemische (Reduktion des freien H^+) und eine chemische (Säure-Base-Gleichgewicht). Annehmend dass: 1. das Oxydo-Reduktions-System H_2/H^+ in Gegenwart von platiniertem Platin rasch ist, und 2. die Gesetze des chemischen Gleichgewichtes in der Nähe der Elektrode gelten, konnten die Versuchsergebnisse erklärt werden.

BIBLIOGRAPHIE

[1] J. COUPEZ, *Anal. Chim. Acta*, 16 (1957) 582.

[2] I. M. KOLTHOFF ET J. J. LINGANE, *Polarography*, Interscience Publishers New York, 1952, p. 243.

[3] P. RÜETSCHI ET G. TRÜMPLER, *Helv. Chim. Acta*, 32 (1952) 1021.

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THE ZIRCONIUM COMPOUNDS OF ETHYLENEDIAMINETETRAACETATE. A HETEROMETRIC STUDY

by

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INTRODUCTION

The object of this paper is to study heterometrically the behaviour and composition of EDTA-metal complexes, which are less than usually soluble in water. We were interested in studying the different intermediates that are formed, and hoped thereby to obtain a better insight into the structural problems of EDTA-complexes. Till now the main interest has centered on the stable and soluble simple complex of EDTA (= E) only. It corresponds to a 1 to 1 ratio of Zr : EDTA.

Volumetric methods using indicators and spectrophotometric titrations of zirconium with EDTA were worked out. The complex, which was obtained at pH 1.3-1.5, appeared to be very strong. Thus ions of Cu^{+2}, Ni^{+2} and Pb^{+2} did not interfere with the reaction of zirconium with EDTA[1]. We present here a heterometric study of the composition and structure of the zirconium-EDTA compounds obtained by us. The compounds described in this work are, at least at first sight, of a rather complex nature, although many of them were also obtained quantitatively in solution. Zirconium itself presents a specific problem as to the nature of the cation which participates in complex formation. We are certain that zirconium acts at all pH's between 1 and 7 as a ***bimetallic*** group, $[Zr_2O]^{+6}$, and not as $[ZrO]^{+2}$ as previously believed. This view was fully supported by the results of this work. It even presents a clue for the understanding of the composition and structure of the compounds identified by heterometry.

EXPERIMENTAL

Apparatus and procedure

The same working conditions were observed as in previous heterometric studies[2]. The fundamentals of heterometry have already been presented briefly previously[3]. All experiments were carried out at 20°C. The temperature of the reaction vessel was thermostatically controlled while the stirring velocity was regulated electronically.

Reagents

Stock solutions of zirconium nitrate and Na_2H_2EDTA were prepared by weighing out the following salts: zirconium nitrate purified, $ZrO(NO_3)_2 \cdot 2H_2O$ Fisher Laboratory Chemical and $Na_2H_2EDTA \cdot 2H_2O$ Eastman Kodak, for chemical purposes. Both the zirconium stock solution and the EDTA were 0.2*M*. Solutions of the required concentrations were prepared by dilution.

All other chemicals were either Analar or chemically pure Baker reagents.

RESULTS

Titrations of zirconium nitrate with EDTA. Many such titrations were carried out. We present in Fig. 1 the composition and the results of a small selection of titrations which were carried out at pH's 1-7. In these experiments our main attention was directed to a study of the composition of the *insoluble* compounds while the titrations shown in Fig. 3 were carried out for the purpose of determining the composition of the soluble compounds. The titration time in each case is also given in the figures.

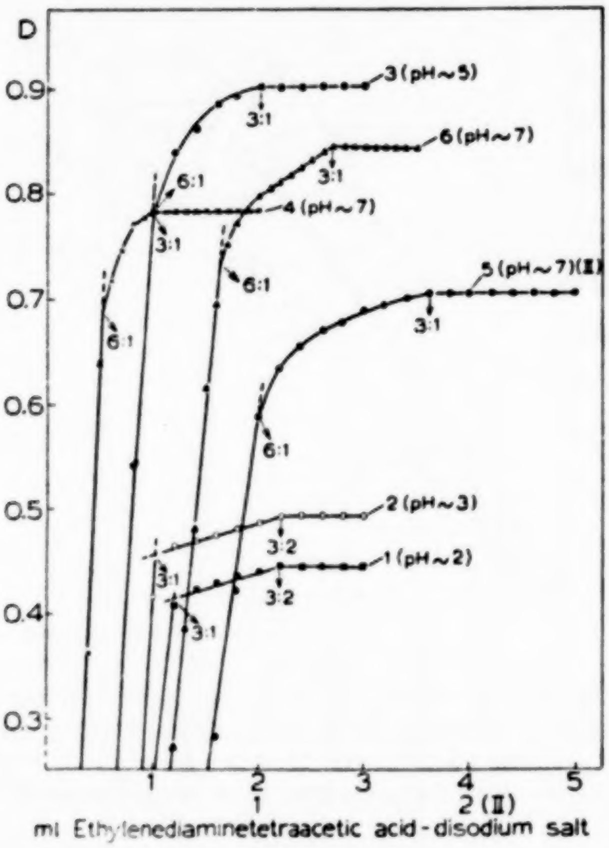

Fig. 1

1. 3 ml $ZrO(NO_3)_2$ 0.1*M* + 1 ml HNO_3 0.1*M* + 16 ml H_2O + *x* ml Na_2H_2EDTA 0.1*M* (35′).
2. 3 ml $ZrO(NO_3)_2$ 0.1*M* + 1 ml CH_3COOH *M* + 16 ml H_2O + *x* ml Na_2H_2EDTA 0.1*M* (31′).
3. 3 ml $ZrO(NO_3)_2$ 0.1*M* + 2 ml CH_3COOH *M* + 2 ml CH_3COONa *M* + 13 ml H_2O + *x* ml Na_2H_2EDTA 0.05*M* (39′).
4. 3 ml $ZrO(NO_3)_2$ 0.1*M* + 1 ml CH_3COONa *M* + 16 ml H_2O + *x* ml Na_2H_2EDTA 0.1*M* (15′).
5. 3 ml $ZrO(NO_3)_2$ 0.1*M* + 1 ml CH_3COONa *M* + 16 ml H_2O + *x* ml Na_2H_2EDTA 0.05*M* (19′).
6. 3 ml $ZrO(NO_3)_2$ 0.1*M* + 1 ml CH_3COONa *M* + 16 ml H_2O + *x* ml Na_2H_2EDTA 0.0333*M* (11′).

The curves show the course of the titrations. The calculated molar ratios of Zr to EDTA at the critical points may also be taken from the curves. The curves of Fig. 1 can be divided into two groups: those obtained at pH's 5-7 and those obtained at pH's 2-3. At pH's 5-7 we obtained the following sequence of reactions (curves 3-6):

$$(1) > \mathrm{Zr} + x\mathrm{E} \rightarrow \ldots 6:1 \downarrow \rightarrow 3:1 \downarrow\downarrow \quad (\mathrm{pH} \sim 5\text{-}7)$$

The compound Zr_3E_1 was not influenced by the addition of more EDTA.

At pH's 2-3 we obtained the following sequence of reactions:

$$(2) > \mathrm{Ze} + x\mathrm{E} \rightarrow \ldots 3:1 \downarrow \rightarrow 3:2 \downarrow\downarrow \quad (\mathrm{pH} \sim 2.3)$$

We thus see that the final compounds obtained at low pH's contain twice as much EDTA as those obtained at higher pH's.

Titrations of EDTA with zirconium nitrate. Fig. 2 presents the composition and results of a small selection of experiments which were carried out at various pH's. With the exception of Expt. 1, which was carried out at pH ∿ 1, the precipitations began immediately on the addition of the first drops of zirconium. At pH ∿ 1 the initial precipitation always occurred at the point of the molar ratio of 1 : 1 (= Zr_1E_1). As to the other critical points, they were almost independent of the pH of the solution. The first maximum optical density point was always obtained either at the ratio of 3 : 1 or 4 : 1. The courses of the reactions were as follows:

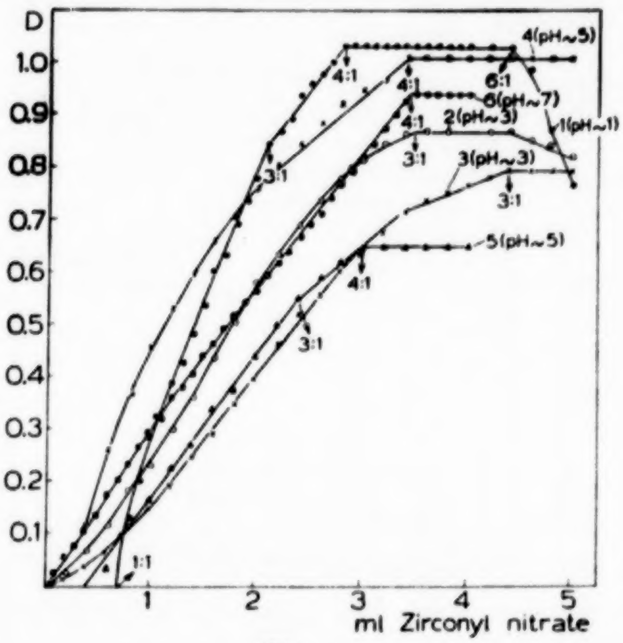

Fig. 2

1. 3 ml Na_2H_2EDTA 0.025M + 2 ml HNO_3 M + 15 ml H_2O + x ml $ZrO(NO_3)_2$ 0.1M (85′).
2. 3 ml Na_2H_2EDTA 0.02M + 2 ml CH_3COOH M + 15 ml H_2O + x ml $ZrO(NO_3)_2$ 0.05M (20′).
3. 4 ml Na_2H_2EDTA 0.01M + 2 ml CH_3COOH M + 14 ml H_2O + x ml $ZrO(NO_3)_2$ 0.025M (30′).
4. 3 ml Na_2H_2EDTA 0.025M + 2 ml CH_3COONa M + 2 ml CH_3COOH M + 13 ml H_2O + x ml. $ZrO(NO_3)_2$ 0.1M (30′).
5. 3 ml Na_2H_2EDTA 0.00625 M + 2 ml CH_3COOH M + 2 ml CH_3COONa M + 13 ml H_2O + x ml $ZrO(NO_3)_2$ 0.025M (33′).
6. 3 ml Na_2H_2EDTA 0.025M + 1 ml CH_3COONa M + 16 ml H_2O + x ml $ZrO(NO_3)_2$ 0.1M (28′).

$$\text{(3a)}\quad (\text{pH} \backsim 1) > E + x\text{Zr} \rightarrow \quad 1:1\uparrow \rightarrow 3:1\downarrow \rightarrow 4:1\downarrow\downarrow$$
$$\text{(3b)}\quad (\text{pH} \backsim 3) > E + x\text{Zr} \rightarrow \ldots 3:1\downarrow\downarrow$$
$$\text{(3c)}\quad (\text{pH} \backsim 5) > E + x\text{Zr} \rightarrow \ldots 3:1\downarrow \rightarrow 4:1\downarrow\downarrow$$
$$\text{(3d)}\quad (\text{pH} \backsim 7) > E + x\text{Zr} \rightarrow \ldots 4:1\downarrow\downarrow$$

The reaction is approximately twice as sensitive at pH's 5-7 than at pH's 1-3.

THE SOLUBLE COMPOUNDS

Many titrations were carried out by us for the purpose of determining the composition of the compounds which were formed nearly quantitatively in solution. This was important, since we wished to obtain information as to whether the insoluble compounds obtained before may also exist in solution. At first, titrations of EDTA were carried out using zirconium nitrate at titrant. It was found that even a 0.001M solution of EDTA gave a precipitate almost immediately when titrated with zirconium nitrate.

As already stated, only in strong mineral acid solution could the soluble compound Zr_1E_1 be obtained (Fig. 2 curve 1). Fig. 3 shows a selection of such titrations carried out at various pH's, using EDTA as titrant. Titrations were repeated using EDTA of various molar concentrations. As we see, the sensitivity of the reaction depends largely on the concentration of the titrant: the higher the concentration the higher the maximum density values obtained. The pH of the titrated solution also influenced the maximum density values (compare Fig. 1 curve 4 with Fig. 3 curve 1). The higher the pH the higher were the maximum densities. From the curves of Fig. 3 we may infer that the points of the initial precipitation coincide with molar ratios of either 4 : 1 or 3 : 1 indicating that the compounds Zr_4E_1 and Zr_3E_1 are quantitatively dissolved. From Fig. 2 (and Fig. 1) we learn that compounds of the same composition were usually obtained as insoluble compounds. We may therefore conclude that under suitable working conditions *the insoluble compounds obtained before, may exist quantitatively in solution*. The structures which were developed later are, therefore, not confined to the solid state, but may well be formed in solution.

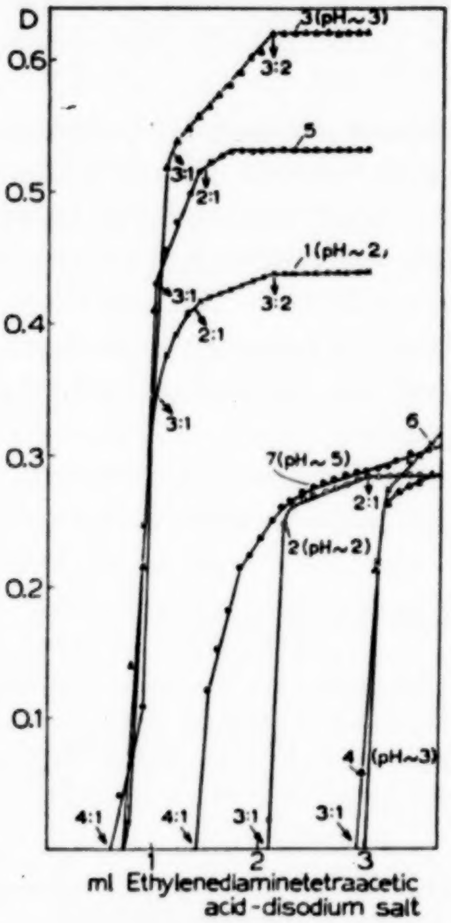

Fig. 3.

1. 3 ml 0.1M $ZrO(NO_3)_2$ + 1 ml 0.1M HNO_3 + 16 ml H_2O + x ml 0.1M Na_2H_2EDTA. 24′
2. 3 ml 0.1M $ZrO(NO_3)_2$ + 1 ml 0.1M HNO_3 + 16 ml H_2O + x ml 0.05M Na_2H_2EDTA. 25′
3. 3 ml 0.1M $ZrO(NO_3)_2$ + 1 ml M CH_3COOH + 16 ml H_2O + x ml 0.1M Na_2H_2EDTA. 18′
4. 3 ml 0.1M $ZrO(NO_3)_2$ + 2 ml M CH_3COOH + 15 ml H_2O + x ml 0.0333M Na_2H_2EDTA. 30′
5. 3 ml 0.1M $ZrO(NO_3)_2$ + 17 ml H_2O + x ml 0.1M Na_2H_2EDTA. 25′
6. 3 ml 0.1M $ZrO(NO_3)_2$ + 17 ml H_2O + x ml 0.0333M Na_2H_2EDTA. 32′
7. 3 ml 0.0125M $ZrO(NO_3)_2$ + 2 ml M CH_3COOH + 2 ml M CH_3COONa + 13 ml H_2O + x ml 0.00625M Na_2H_2EDTA. 40′.

From Fig. 3 we also conclude that the compound Zr_4E_1 can be obtained in solution at various pH's; however, if the titrant was more dilute, the compound obtained has the composition Zr_3E_1.

DISCUSSION

Analysing the results, we were surprised by the variety of compounds formed quantitatively either as final or as intermediate products and which were transformed into one another.

The ratios of zirconium to EDTA in the compounds were as follows:

$$1:1\uparrow,\ 3:2\downarrow,\ 2:1\downarrow,\ 3:1\uparrow\downarrow\ 4:1\downarrow\uparrow,\ 6:1\downarrow$$

The compound Zr_1E_1 was soluble and was transformed into other compounds by further addition of zirconium according to reaction (3a). Already in a previous investigation[4] of the reaction of zirconium with oxalic acid we came to the conclusion that zirconium nitrate in aqueous solution acts in the pH range of 1-7 as the condensed group $[Zr_2O]^{+6}$. Reaction (3a) as well as all other reactions studied can then be reasonably explained and the sequence of compounds obtained becomes understandable. We have only to disregard the ionic charges and direct our main attention to the structure of the Zr-EDTA-skeleton in each compound reported.

Reaction (3a) as well as all other reactions occurring in the pH range of 1-3 when a solution of zirconium is added dropwise to a solution of EDTA, can be represented as follows:

$$(4)\quad 2\,E + [Zr_2O]^{+6} \rightarrow \underset{(a)}{E.Zr_2O.E}\uparrow \left(= \begin{matrix}E.Zr\\ E.Zr\end{matrix}\!\!>O\right)\ (1:1)$$

$$(5)\quad E.Zr_2O.E. + 2\,[Zr_2O]^{+6} \rightarrow \underset{(b)}{Zr_2O.E.Zr_2O.\,E.Zr_2O}\downarrow\ (3:1)$$

$$(6)\quad Zr_2O.E.Zr_2O.E.Zr_2O + [Zr_2O]^{+6} \rightarrow 2\,\underset{(c)}{Zr_2O.E.Zr_2O}\downarrow\downarrow\ (4:1)$$

In the reverse titration we obtained at pH's 1-3 the sequence of compounds shown in equation (2). There is no doubt that the compound 3 : 1↓ was not the primary reaction product. The reaction occurred after the addition of a minimum quantity of EDTA and probably we obtained compounds which were transformed into each other. We may therefore represent reaction (2) as follows:

$$(7)\quad 2\,[Zr_2O]^{+6} + E \rightarrow \underset{(c)}{Zr_2O.E.Zr_2O}\downarrow\ (4:1)$$

$$(8)\quad 3\,Zr_2O.E.Zr_2O + E \rightarrow 2\,\underset{(b)}{Zr_2O.E.Zr_2O.E.Zr_2O}\downarrow\ (3:1)$$

$$(9)\quad Zr_2O.E.Zr_2O.E.Zr_2O + 2\,E \rightarrow \underset{(d)}{E.Zr_2O.E.Zr_2O.E.Zr_2O.E.}\downarrow\downarrow\ (3:2)$$

At pH's 5-7 we obtained the sequence of compounds shown in equation (1).

The reaction (1) may be represented as follows:

$$(10)\quad 3\,[Zr_2O]^{+6} + E \rightarrow \underset{(e)}{[E.(Zr_2O)_3]}\downarrow \left(= \begin{matrix} & Zr_2O & \\ & \vdots & \\ Zr_2O\cdot & E & \cdot Zr_2O\end{matrix}\right)\ (6:1)$$

$$(11)\quad E(Zr_2O)_3 + E \rightarrow \underset{(b)}{Zr_2O.E.Zr_2O.E.Zr_2O}\downarrow\downarrow\ (3:1)$$

Since EDTA has at most six coordination points, it follows that not more than *three* Zr_2O-groups can be chelated by *one* molecule of EDTA. In all probability all these compounds can also be obtained in solution and be transformed into each other. The structures "b", "c" and "d" seem to be the most probable. The composition of the final compound (= ↓ ↓) in each sequence of reactions depends on the pH of the titrated solution as well as on the titrant used. Thus titrating with EDTA we obtained at pH's 2-3 the final compound "d" while at pH's 5-7 the final compound "b" was obtained. On the other hand, on titrating with zirconium as titrant we obtained at almost all pH's the final compound "c". As many of the compounds described before do exist in acid solution, even in mineral acid solution, it is clear that the titration of zirconium with EDTA can be successful only under very restricted conditions and concentrations of the components.

SUMMARY

The compounds formed at pH's 1-7 between zirconium and ethylenediaminetetraacetate (= E) were studied. The following soluble or insoluble compounds were obtained either as intermediates or as final compounds:

$Zr_1E_1 \uparrow$, $Zr_3E_2 \downarrow$, $Zr_2E_1 \downarrow$, $Zr_3E_1 \downarrow\uparrow$, $Zr_4E_1 \uparrow\downarrow$ and $Zr_6E_1 \downarrow$.

The composition and sturcture of the compounds and the reactions occurring were discussed.

RÉSUMÉ

Les auteurs ont étudié les composés formés entre le zirconium et l'éthylènediaminetétraacétate de sodium (= E) aux pH de 1 à 7. Les composés suivants finals ou intermédiaires, solubles ou insolubles ont été obtenus:

$Zr_1E_1 \uparrow$, $Zr_3E_2 \downarrow$, $Zr_2E_1 \downarrow$, $Zr_3E_1 \downarrow\uparrow$, $Zr_4E_1 \uparrow\downarrow$, et $Zr_6E_1 \downarrow$.

La composition et la structure des composés et les réactions produites sont discutées

ZUSAMMENFASSUNG

Die Verbindungen, welche zwischen Zirkonium und Äthylendiamintetraacetat bei pH 1-7 gebildet werden, wurden studiert. Die folgenden löslichen sowie unlöslichen Verbindungen wurden als Zwischen- oder Endverbindungen erhalten:

$Zr_1E_1 \uparrow$, $Zr_3E_2 \downarrow$, $Zr_2E_1 \downarrow$, $Zr_3E_1 \downarrow\uparrow$, $Zr_4E_1 \uparrow\downarrow$ und $Zr_6E_1 \downarrow$.

Die Zusammensetzung und Struktur der Verbindungen sowie die stattfindenden Reaktionen wurden diskutiert.

REFERENCES

[1] S. G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 31 (1948) 459.
G. W. C. Milner and P. J. Phennah, *Analyst*, 79 (1954) 475.
Philip B. Sweetser and Clark E. Bricker, *Anal. Chem.*, 26 (1954) 196.
James S. Fritz and Myron O. Fulda, *Anal. Chem.*, 26 (1954) 1206.

[2] See literature on heterometry 1953-1956 in *Anal. Chim. Acta*, 15 (1956) 62.
M. Bobtelsky and B. Mayer, *Anal. Chim. Acta*, 15 (1956) 164, 373.
M. Bobtelsky and E. Jungreis, *J. Inorg. Nucl. Chem.*, 2 (1956) 38.
M. Bobtelsky and R. Rafailoff, *Anal. Chim. Acta*, 15 (1956) 457; 16 (1957) 488; 17 (1957) 479.
M. Bobtelsky and I. Yulius, *Anal. Chim. Acta*, 16 (1957) 75.
M. Bobtelsky and J. Eisenstadter, *Anal. Chim. Acta*, 16 (1957) 479.

[3] M. Bobtelsky, *Anal. Chim. Acta*, 13 (1955) 172.

[4] M. Bobtelsky and A. Ben-Bassat (to be published shortly).

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THE PHOTOMETRIC TITRATION OF NICKEL IN THE PRESENCE OF COBALT

by

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The present paper deals with the spectrophotometric titration of nickel(II) with the disodium salt of ethylene diamine tetraacetic acid (versenate) in the presence of cobalt-(II) by a modification of a method suggested by SWEETSER AND BRICKER[1] for nickel alone. The corrected absorbancy is plotted against milliliters of titrant added which results in straight lines intersecting at the end-point. The effects of pH, concentrations and limitations of the method are presented. The merits of spectrophotometric titrations have already been covered adequately in the literature by other investigators[2,3,4].

APPARATUS

A Beckman Model B spectrophotometer with a special cell compartment was used for all titrations. The titration cell and cell compartment proposed by SWEETSER AND BRICKER[1] was modified and improved as shown in Fig. 1. The T-shaped cell was constructed from borosilicate glass with a 7 cm light path and 3.8 cm diameter.

Stray light was excluded from the cell compartment by painting the neck of the titration cell with flat black paint and by fitting the titration cell with a cover as shown in Fig. 1. The cover, consisting of a felt disk between two brass disks, had two holes to accommodate the stirring rod and buret. The cover was held firmly on the titration cell by three spring clamps. A metal cover and rubber gasket was constructed for the cell compartment to accommodate the titration cell and to exclude stray light.

REAGENTS

Standard 0.1M and 0.03M versenate — Disodium dihydrogen ethylene diamine tetraacetate dihydrate (reagent grade) obtained from the J.T. Baker Chemical Co. was dissolved in water and standardized against a standard nickel solution.

Nitroso-R salt solution — 10 g of reagent grade nitroso-R salt (1-nitroso-8-naphthol-3,6-disulfonic acid disodium salt) obtained from Fisher Scientific Co. was dissolved in water and diluted to 1 liter. The solution was stored in the dark.

Sodium acetate solution — 500 g of anhydrous sodium acetate was dissolved in 1 liter of water.

Sodium hydroxide — Saturated solution.

Nitric acid 8N.

Standard nickel solution — 0.6 g of pure nickel obtained from Johnson, Matthey and Co., London, was dissolved in dilute nitric acid and diluted to 1 liter.

PROCEDURE

Standardization of versenate

Pipet 25 ml of the standard nickel solution into a 150 ml beaker for the standardization of the 0.1M versenate and proceed as described in the determination of nickel in the presence of cobalt. For the 0.03M versenate, 10 ml of the standard nickel is used.

Determination of nickel in the presence of cobalt

To the nickel solution containing cobalt which has been concentrated to 30 ml in a 150 ml beaker, add 10 ml of sodium acetate solution and 40 ml of the nitroso-R salt solution. Adjust the pH of the solution to between 5 and 7 with sodium hydroxide to promote the formation of the cobalt complex. Allow to stand for 10 minutes. Heat the solution until it begins to boil and immediately add 10 ml of 8N nitric acid. Continue heating for exactly 20 seconds. Remove and cool rapidly to room temperature with stirring in an ice bath. Place the samples in the dark until ready to titrate. Adjust the pH between 3.5 and 4.0 with saturated sodium hydroxide. Transfer the solution to the titration cell and dilute to a volume of 120 ml. Immerse the stirring rod and tip of buret into the solution. Set the wave length at 1000 mμ and adjust the slit width between 0.0 to 0.05 on the absorbancy scale with the sensitivity selector set at position 3. Titrate with standard versenate and record the absorbancy at 0.0, 0.3, 0.6, 1.0 and every 0.5 ml until at least three readings are taken beyond the end-point.

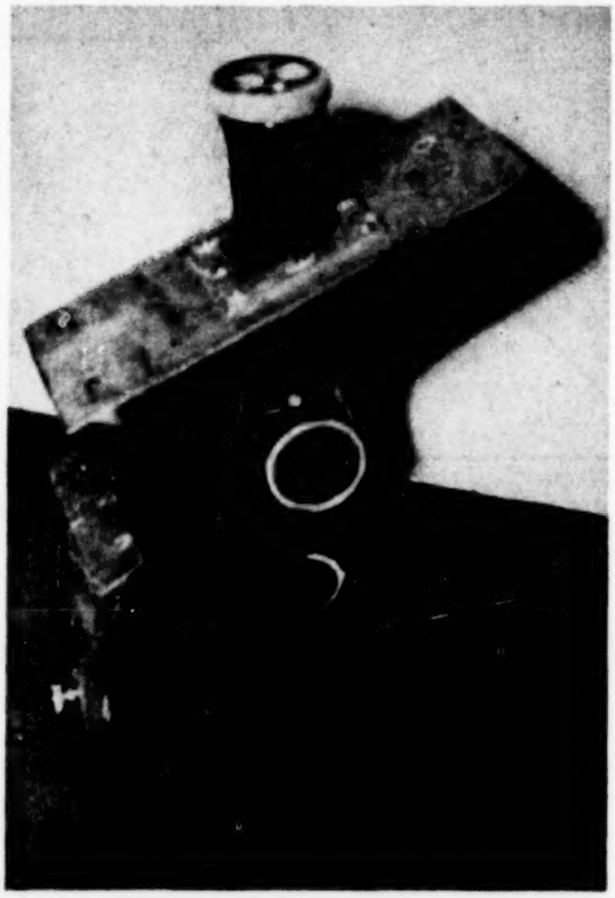

Fig. 1. Titration cell and cell compartment for a Beckman Model B Spectrophotometer.

The end-point is found when the absorbancy, corrected for dilution, is plotted against the ml of titrant. The absorbancy is corrected for dilution by multiplying the observed absorbancy by the correction factor (A + B/A) where A is the original volume of solution being titrated and B is the volume of titrant added at a given observed absorbancy. This plot results in two straight lines which intersect and indicates the end-point. A typical titration curve is shown in Fig. 2.

The 0.03M versenate solution is used when the nickel concentration is between 2.5 and 9.0 mg and the 0.1M versenate for nickel concentrations between 7.5 and 25 mg.

RESULTS AND DISCUSSION

The results in Table I and Table II show that versenate can be applied successfully to the determination of nickel in the presence of cobalt. Nickel forms a stable chelate with versenate at a pH of 3.5 to 4.0 and can be titrated photometrically at 1000 mμ.

At this wave length the nickel versenate chelate absorbs strongly. At a higher or lower pH, chelation is slow and often incomplete until a large excess of versenate is added. The cobalt is masked by complexing it with nitroso-R salt. The cobalt will not interfere with the titration of nickel because it can not be chelated by the versenate and the red colored cobalt complex does not absorb. Cobalt forms a very stable complex with excess nitroso-R salt in a sodium acetate buffered solution at a pH of 5.0 to 7.0[5]. Nickel is complexed also by nitroso-R salt under these conditions but the nickel complex and the excess nitroso-R salt are destroyed when nitric acid is added to the boiling solution. Excessive heating, longer than 25 seconds, after the addition of the nitric acid gives high results for nickel due to the decomposition of the cobalt nitroso-R salt complex. On the other hand, heating for less than 15 seconds gives low results for nickel because all of the nickel is not liberated from the nitroso-R salt complex.

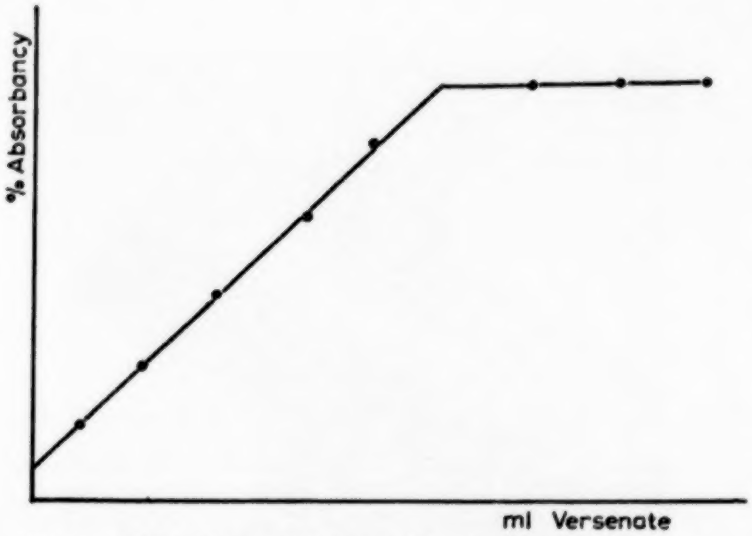

Fig. 2. Titration of nickel with standard versenate.

TABLE I

DETERMINATION OF NICKEL WITH 0.1M VERSENATE IN THE PRESENCE OF COBALT

Cobalt taken *mg*	*Nickel taken* *mg*	*Nickel found* *mg*	*Error* %
4	7.45	7.51	0.8
5	7.45	7.42	0.4
7	7.45	7.48	0.4
4	14.96	14.98	0.1
6	14.96	15.01	0.3
7	14.96	14.89	0.5
4	22.41	22.19	1.0
6	22.41	22.45	0.2
7	22.41	22.45	0.2

Concentrations of 6 to 25 mg of nickel were determined in the presence of up to 7.0 mg of cobalt with an error not greater than one per cent (0.1M versenate). The determination of 2.5 to 9.0 mg of nickel in the presence of up to 8 mg of cobalt may result in an error not greater than one and a half per cent (0.03M versenate). Up to 4 mg of manganese(II) or tin(IV) does not interfere in the determination of nickel. The presence of silver(I), copper(II), iron(III), vanadium(V) and (IV), chromium(III), zinc(II), and aluminum(III) interfere and will cause high results.

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TABLE II

DETERMINATION OF NICKEL WITH 0.03*M* VERSENATE IN THE PRESENCE OF COBALT

Cobalt taken mg	*Nickel taken* mg	*Nickel found* mg	*Error* %
5	2.77	2.81	1.4
6	2.77	2.80	1.1
7	2.77	2.81	1.4
8	2.77	2.79	0.7
5	5.45	5.50	0.9
6	5.45	5.51	1.0
3	5.93	5.94	0.2
7	5.93	5.89	0.7
8	5.93	5.99	1.0
5	8.88	8.82	0.7
6	8.88	8.96	0.9
7	8.88	8.93	0.6
8	8.88	8.87	0.1

ACKNOWLEDGEMENT

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SUMMARY

A spectrophotometric titration of nickel in the presence of cobalt is described using disodium ethylene diamine tetraacetic acid as a titrant. The end-point was obtained by plotting the corrected absorbancy against ml of titrant added. Nickel concentrations of 2.5 to 25 mg were determined in the presence of up to 8 mg of cobalt with an error of 1½% or less depending upon the concentration of versenate used. A 0.03*M* and 0.1*M* versenate was used. The effects of pH, concentrations of nickel and cobalt, accuracy of the method, presence of interfering elements, and limitations of the method are discussed.

RÉSUMÉ

Un titrage spectrophotométrique est décrit pour le dosage du nickel en présence de cobalt, au moyen de l'éthylènediaminetétracétate disodique comme réactif. Le point final est obtenu en rapportant l'absorption corrigée au volume de réactif ajouté. Des quantités de nickel de 2.5 à 25 mg ont pu être dosées en présence de quantités de cobalt allant jusqu'à 8 mg, avec une erreur de 1.5% ou moins, suivant la concentration de versénate utilisée. Des solutions de versénate 0.03*M* et 0.1*M* ont été employées. L'influence du pH, les concentrations de nickel et de cobalt, la précision de la méthode, la présence d'éléments gênants et les limites de la méthode sont discutées.

ZUSAMMENFASSUNG

Die spektrophotometrische Titration von Nickel in Gegenwart von Kobalt mit Dinatrium-äthylendiamintetraacetat als Titriermittel wurde beschrieben. Der Endpunkt wurde erhalten durch Aufzeichnen der korrigierten Absorption gegen die zugefügte Anzahl ml des Titriermittels. Nickelkonzentrationen von 2.5 bis 25 mg wurden in Gegenwart von bis zu 8 mg Kobalt mit einem Fehler von 1.5% oder weniger in Abhängigkeit von der verwendeten Versenatkonzentration bestimmt. 0.03*M* und 0.1*M* Versenat wurde verwendet. Die Auswirkung des pH, die Konzentrationen von Nickel und Kobalt, die Genauigkeit der Methode, die Gegenwart störender Elemente und die Grenzen der Methode wurden erörtert.

REFERENCES

[1] P. B. Sweetser and C. E. Bricker, *Anal. Chem.*, 25 (1953) 253.

[2] R. F. Goddu and D. N. Hume, *Anal. Chem.*, 26 (1954) 1740.

[3] P. B. Sweetser and C. E. Bricker, *Anal. Chem.*, 26 (1954) 195.

[4] H. V. Malmstadt and E. C. Gohrbandt, *Anal. Chem.*, 26 (1954) 442.

[5] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., New York, 1950, p. 274.

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FAST GREY RA AS A NEW COLORIMETRIC REAGENT FOR THE MICRODETERMINATION OF BISMUTH

by

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In a previous investigation[1] the azo dye Fast Grey RA has proved to be a suitable indicator for volumetric estimation of bismuth with EDTA. The reddish-violet colour of the Fast Grey bismuth compound can be used as a basis for colorimetric microdetermination of this metal. Among the colorimetric methods cited in the literature for the microdetermination of bismuth are those that make use of EDTA[2], and diethyldithiocarbamate[3].

EXPERIMENTAL

Compounds: All the chemicals used in this investigation were of the required purity. The water used was always twice distilled.

Solutions: The bismuth solution was prepared and standardised as previously mentioned[1]. A stock solution containing 100 μg bismuth per ml was prepared by the appropriate dilution, with 0.01 N nitric acid solution, from a more concentrated previously standardised one. Further dilutions were prepared from this stock solution.

Reagent: An aqueous solution of the dye is prepared by dissolving the calculated amount in the appropriate volume of pure water.

Effect of pH: The reddish-violet bismuth-Fast Grey compound was developed in a series of concentrations of 0.2, 0.1, 0.05, 0.02 and 0.01N nitric acid, by pipetting 1 ml (50 μg Bi), 5 ml acid solution, 1 ml 0.1% reagent, and finally water up to the mark in 10 ml volumetric flasks. The best colour was developed at pH 2 and 3.

Alcohol and acetone are found to be without influence on the colour of the F.G.-Bi compound.

Selection of the suitable wavelength: By measuring the absorbance of a coloured solution containing 50 μg Bi per 10 ml against its blank (difference curve) with a recording Beckman spectrophotometer, a peak is observed, corresponding to a maximum absorbancy at a wavelength of 570 mμ.

Molecular structure of the F.G.-Bi compound: F.G. is an azo dye (metahydroxy-1-naphthylazo-2-hydroxy-3-nitrobenzene-5-sulphonic acid) with the formula $C_{16}H_{11}O_7N_3S$. In order to investigate the molecular structure of its compound with bismuth, measurements were carried out with a Beckman spectrophotometer of type B with a blue-sensitive photocell and 1 cm cells at a wavelength of 570 mμ using 50 μg cation per 10 ml in the order 1 ml (50 μg Bi) + 4.5 ml 0.02N HNO_3 + increasing volumes of freshly prepared 0.01% reagent + water up to 10 ml and pure water as the blank. Representative results are listed in Table I.

TABLE I

Reagent in ml	1	2	2.5	2.75	3	4
Absorb.	0.14	0.225	0.272	0.29	0.30	0.33
Trans.	72.5	59.5	53.5	51.0	50.0	47.0

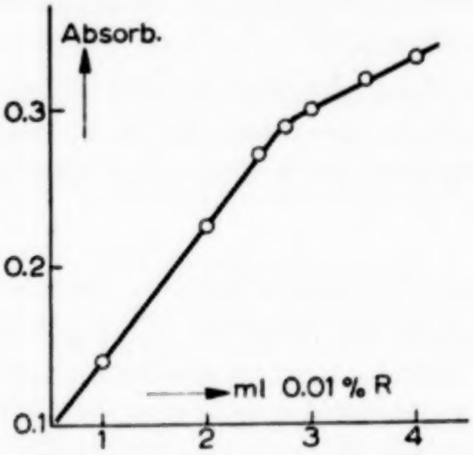

Fig. 1. Absorbance versus reagent concentration.

From the above data and the corresponding Fig. 1 it is apparent that the amount of 0.01% reagent required to react quantitatively with 50 μg Bi, per 10 ml is $\sim$2.8 ml, from which the molecular weight of the dye is calculated to be 390 on the basis that the dye is monobasic, which is the case. This value is in excellent agreement with the exact value of 389.34 suggesting thus a molecular structure of one mole of bismuth and three moles of the dye.

Sensitivity and sequence of additions: Sensitivity of the method is tested by measurements with a Lange photometer, model VI, connected to a galvanometer on which 200 divisions correspond to 50% absorbancy. It is easily possible to determine 0.1 p.p.m. of Bi using a cell of a light-path of about 34 mm and a capacity of about 5 ml. On the other hand it is possible to carry out measurements with the Beckman Spectrophotometer starting from 5 p.p.m. and hence to determine such on amount by using a Beckman instrument.

In order to test the influence of a variation of the sequence of addition of the constituents in presence of which the coloured F.G.-Bi compound is developed, measurements were carried out with the Beckman instrument which led to the conclusion that the suitable sequence of addition is the following one: bismuth solution, nitric acid solution, reagent and water.

Effect of time: By measuring the absorbancy of a number of solutions involving, 10, 30 and 50 μg Bi per 10 ml, 5, 10, 20, 30 and 40 minutes after addition of the reagent, it is concluded that such solutions are stable within 20 minutes after preparation and thereafter, the colour begins to fade slowly with time. On the other hand, coloured solutions containing from 1 to 10 μg Bi per 10 ml are stable for several hours.

Influence of temperature: Measurements can be carried out between 15 and 30°C without any appreciable deviations.

Influence of foreign cations: Preliminary tests are carried out in test tubes each containing 1 ml of a bismuth solution equivalent to 10 μg. Then starting from the second test tube, different cations are added either in solution of known acidity and content or as solid, containing 10 to 100 fold the amount of bismuth. $0.02N$ NHO_3 is then added, so as to bring the solution in all test tubes to the same acidity, followed by 1 ml of 0.01% reagent. The volume is made up to 10 ml with water and the contents well mixed. By comparing the developed colours with that of the first tube containing pure bismuth solution, the conclusion is drawn that cations of the alkaline and the rare-earths, except zirconium, Al, Co, Zn, Hg^+, Pb and U in at least 10-fold the amount of bismuth do not interfere with its determination. Among the interfering cations are to be mentioned Cu, Ni, Cd, V, Zr and ferric iron. The latter element, however, can be masked to an appreciable extent by reduction to the ferrous state with drops of $0.2M$ ascorbic acid solution.

Influence of foreign anions: By measuring the absorbance of a coloured solution containing 10 μg Bi per 10 ml in the presence of a mixture of the anions of chloride, sulphate, acetate, tungstate, citrate, tartrate and oxalate in at least 10 fold the amount of bismuth the result showed a deviation of less than 10% from that obtained with a pure bismuth solution of the same acidity and bismuth content.

Obeyance of Beer's law: Two sets of measurements are carried out, one covering the range of 1 to 10 μg Bi per 10 ml using the Lange photometer and the other covering the range of 10 to 70 μg Bi per 10 ml using the Beckman spectrophotometer. Both sets of measurements show that the variation of concentration with extinction conforms satisfactorily with Beer's law. Results are represented graphically by the curves A and B in Figs. 2 and 3.

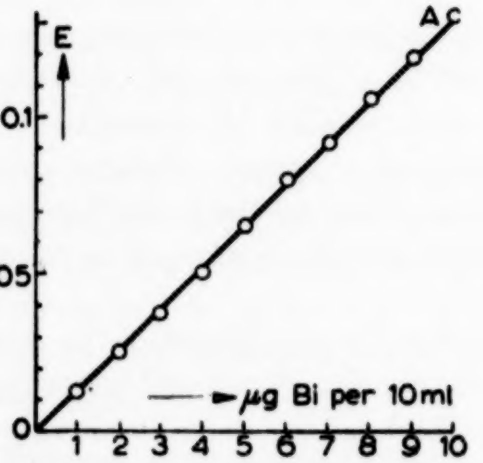

Fig. 2. Extinction versus concentration (Lange photometer).

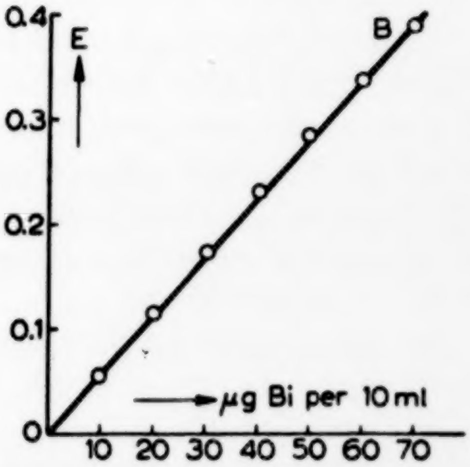

Fig. 3. Extinction versus concentration (Beckman spectrophotometer).

Detailed procedure: 1 ml of the bismuth solution $0.01N$ in respect to nitric acid and containing between 0.1 and 1 or 1 and 7 p.p.m. of bismuth is transferred to a 10 ml volumetric flask. The reagents are pipetted into the flask in the following order, mixing after each addition: 4.5 ml $0.02N$ HNO_3 acid solution, 1 ml 0.01 or 0.1 per cent freshly prepared solution of the reagent, respectively with low and high bismuth concentrations, and finally water up to the mark. The absorbancy is measured against a blank containing the same acid gradients but without bismuth, using the Lange photometer and orange filters with maximum absorbance at 570 mμ or the Beckman spectrophotometer at the same wavelength, with low and high bismuth concentrations respectively. The concentration of bismuth can be read from curves prepared in the same manner from standard Bi solutions, curves A and B in Figs. 2 and 3. Under these conditions, the colour of the F.G.-Bi compound is developed immediately and is stable for several hours with low bismuth concentrations or for 20 minutes with higher ones.

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SUMMARY

Fast Grey RA dye has proved to be a sensitive colorimetric reagent for microdetermination of bismuth. By its aid it is possible to determine with precision concentrations between 0.1 and 1 p.p.m. in the presence of some other cations and anions, with a sensitive photometer or a Beckman spectrophotometer at a wavelength of 570 mμ. Among the interfering elements are cations of Cu, Zr, Ni, Cd, V and ferric iron. The latter element however, can be masked, to a great extent, by reduction with ascorbic acid.

RÉSUMÉ

Le colorant ,,Fast Grey RA'' peut être utilisé comme réactif colorimetrique sensible pour le microdosage du bismuth. Il permet de doser avec précision des concentrations comprises entre 0.1 et 1 p.p.m., en présence de quelques autres cations et anions au moyen d'un photomètre sensible ou d'un spectrophotomètre Beckman, à une longueur d'onde de 570 mμ. Les ions des éléments suivants: Cu, Zr, Ni, Cd, V et Fe(III) gênent. Le fer(III) cependant peut être masqué par réduction au moyen de l'acide ascorbique.

ZUSAMMENFASSUNG

Der Farbstoff Fast Grey RA hat sich als ein empfindliches kolorimetrisches Reagenz für die Mikrobestimmung von Wismuth erwiesen. Mit seiner Hilfe können Konzentrationen von 0.1 und 1 p.p.m. in Gegenwart einiger anderer Kationen und Anionen mit einem empfindlichen Photometer oder einem Beckman-Spektrophotometer bei einer Wellenlänge von 570 mμ genau bestimmt werden. Zu den störenden Elementen gehören Cu, Zr, Ni, Cd, V und Fe(III). Das letztere kann aber grösstenteils durch Reduktion mit Ascorbinsäure getarnt werden.

REFERENCES

[1] H. Khalifa, *Anal. Chim. Acta*, 17 (1957) 194.
[2] P. W. West and H. Coll, *Anal. Chem.*, 27 (1955) 1221.
[3] K. L. Cheng, R. H. Bray and S. W. Melsted, *Anal. Chem.*, 27 (1955) 24.

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STUDIES OF GOLD, PLATINUM AND PALLADIUM INDICATING ELECTRODES IN STRONGLY OXIDIZING AQUEOUS SOLUTIONS

by

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The earliest measurement of redox potentials with a platinum indicating electrode was made by Bancroft[1]. Since then, platinum and other noble metals have been widely used for such measurements. Various mechanisms by which an indicating electrode acquires the solution potential have been proposed[2–4]. All these treatments assumed that the indicating electrode underwent no chemical change. The concept of inertness is still currently accepted even though the possibility of chemical oxidation on the electrode surface has been pointed out by many workers[5].

Recent work in voltammetry by Kolthoff and Tanaka has shown the existence of oxide films on platinum electrodes after being immersed in an oxidizing aqueous solution[5]. Ross and Shain have recorded drifting potential-time curves for platinum indicating electrodes immersed in solutions of various oxidants and reductants. Their result shows that the formation and dissolution of oxide coatings are slow processes. The rates are dependent upon the nature and concentration of the redox species in the solution[6].

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The purpose of the present study is to examine the transient potential-time behavior of a "reduced" indicating electrode. (An electrode is said to be reduced when it is thoroughly pre-treated cathodically to remove all oxidized material on the surface.) The potential-time patterns were compared with well established data from the electrical oxidation of these metals. The results provide substantial evidence that noble metal indicating electrodes undergo stepwise oxidation prior to the establishment of a stable potential.

Redox couples such as Ce^{+4}/Ce^{+3} and MnO_4^-/Mn^{+2} were used in this study because of their common usage. All solutions contained approximately equimolar concentrations of a conjugate redox pair so as to simulate conditions during the measurements of formal potentials. No significance of electrochemical reversibility of poising action is implied.

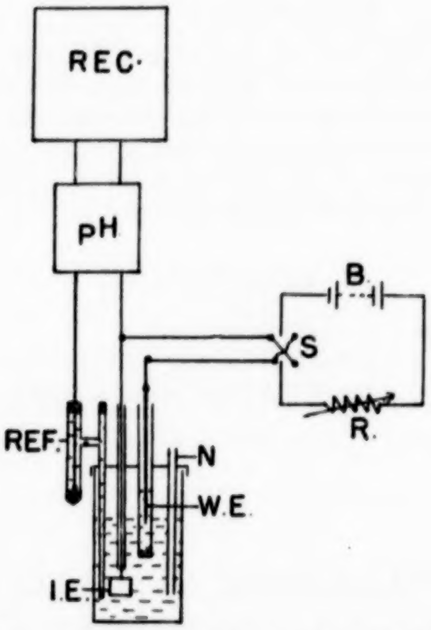

Fig. 1. Apparatus for measuring potential-time curves.

EXPERIMENTAL

General technique

It was desired to obtain a complete picture of the response of a noble metal indicating electrode, beginning with reduced conditions and ending with the attainment of the solution potential. An experimental method was devised so that the electrode could be treated cathodically in a solution containing the selected redox couple. Upon the interruption of the cathodic current, the electrode would be subjected to the chemical oxidation of the soluble redox couple. The recorded potential-time curve thus obtained shows all changes at the electrode during the period desired.

Apparatus

Fig. 1 illustrates the arrangement of the electrolysis cell as well as the potential measuring the recording equipment. The indicating electrode (IE) and the shielded electrode (WE) were connected through a switch (S) to a constant current source comprised of the batteries (B) and the variable resistor (R). The potential of the indicating electrode was monitored with respect to the reference electrode (REF) by means of a Leeds and Northrup Model 7664 pH meter. The output of the pH meter was fed to a Leeds and Northrup Speedomax recorder. The recorder had a 20 mV slidewire, fully adjustable zero and a nominal pen speed of 1 second. The chart speed was 8" per minute.

The indicating electrodes were made of C.P. gold, platinum and palladium foil manufactured by Baker and Co., Neward, N. J. The apparent surface of each electrode was about 8 cm^2.

The reference electrode was a saturated lead amalgam-lead sulfate-1*N* sulfuric acid electrode. The potential of this was —0.265 volts *vs.* the N.H.E. All potentials reported herein are referred to the N.H.E. as reduction potentials. Due to the nature of the measuring and recording instruments, the accuracy of the potential measurements was estimated as ± 10 millivolts.

The shielded electrode consisted of a platinum wire dipping into a solution containing the same electrolytes as in the main electrolysis cell. Provision was made for passing nitrogen through the solution or over the surface by means of lowering and raising the tubing (N).

All solutions were prepared from chemicals of reagent grade and were standardized by conventional methods. Tank nitrogen was used without further purification for deaeration and to provide an oxygen-free atmosphere over the solution.

Procedure

In accordance with common practice, all indicating electrodes were "cleaned" by soaking for 15 minutes in a solution of concentrated sulfuric acid saturated with potassium dichromate. The electrodes were then washed thoroughly with distilled water before use. The electrodes and equipment were arranged as in Fig. 1. The outer vessel as well as the shielded electrode compartment was filled with the desired redox solution, *e.g.* Ce^{+4}/Ce^{+3} in 1*N* sulfuric acid.

A small cathodic current, the magnitude of which should be slightly greater than that of the diffusion current of the reducible species in the solution at the electrode, was passed through the indicating electrode while the shielded electrode served as an anode. The potential of the indicating electrode became more cathodic with time until a relative stable level was reached concurrent with the evolution of hydrogen gas on the surface. The potential at this time was close to that of a normal hydrogen electrode. (The electrode in such a condition is referred to as a "reduced" electrode in the remainder of this paper.) After the indicating electrode was reduced, the electrolysis current was stopped and the recorder turned on simultaneously. A potential-time curve of the indicating electrode was thus obtained. Since the indicating electrodes were subjected to the chromic caid treatment prior to use, a stripping pattern of the "oxidized" electrode could be obtained if the recorder were turned on before starting the electrolysis current.

For comparison purposes, electrolytic oxidations of the electrodes were also carried out. In this case, the electrolysis cell was filled with only the background electrolyte, *e.g.* 1*N* sulfuric acid. After the cathodic pretreatment as described above, an anodic current was passed through the indicating electrode by suddenly reversing the polarity of the switch (S). (All potential-time curves in this paper are original chart paper recordings. In many cases the pen tracings have been inked over for reproduction.)

RESULTS

1. Gold electrode

Fig. 2 is a typical potential-time curve obtained by the chemical oxidation of a reduced gold electrode in 1*N* sulfuric acid solution. The flat portion indicated by A and the pronounced potential holdups at B and D, as well as the small changes of slope at C and E, are highly persistent and reproducible regardless of the redox system used. The overall slope of the potential-time pattern as well as the magnitude of the potential holdups is dependent upon the nature and concentration of the redox pairs.

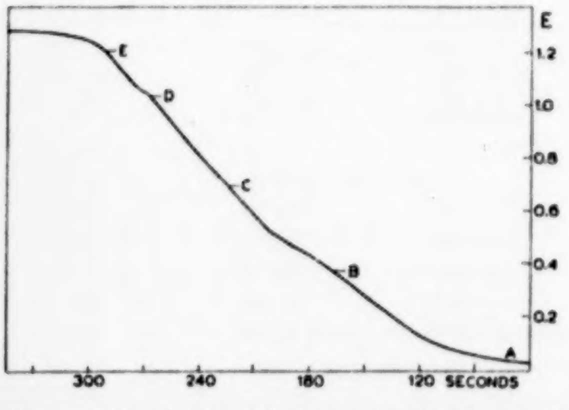

Fig. 2. Chemical oxidation of gold electrode by permanganate in 1*M* sulfuric acid.

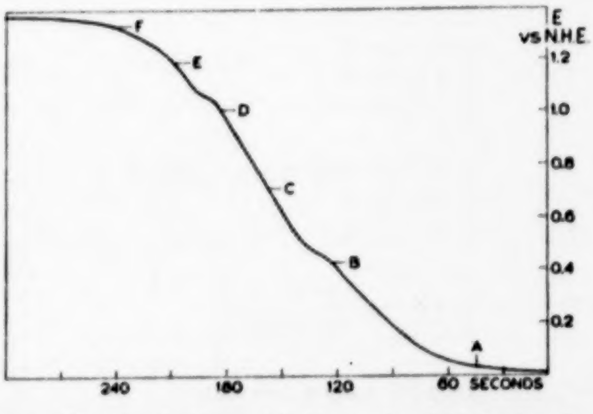

Fig. 3. Electrolytic oxidation of gold electrode in sulfuric acid.

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The inflections and holdups on the potential-time curves must be due to reactions at the electrode surface since they are independent of the chemical species in the solution. These reactions were suspected to be the stepwise oxidation of the electrode material. Electrolytic oxidation studies of noble metals have established considerable information on oxide film formation on electrode surfaces[7-9]. Rather than comparing the chemical oxidation directly with the existing literature date, it was felt that more valid conclusions might be drawn by carrying out anodic oxidation of the same electrode under comparable conditions.

Fig. 3 is a typical potential-time curve obtained from the electrolytic oxidation of the gold electrode in 1*N* sulfuric acid. In accord with the well-documented interpretations of previous workers[8], the initial flat portion A can be attributed to the desorption and oxidation of hydrogen on the electrode. The potential holdups B and D, as well as the change of slope at E, are due to the formation of various oxides. Evolution of oxygen commences at F. The slight but consistent change of slope at C is relatively unimportant in acid solution. As observed by previous workers[8], this step becomes a major potential holdup in alkaline media. This is believed to be the dissolution of gold. It should be emphasized that the present work, like that of the previous workers, does not distinguish between oxide, hydroxide or hydrated oxide.

The results of the chemical oxidation of the gold electrode using several redox couples at various concentrations are summarized in Table I. The potential at the mid-point of a potential holdup should represent the formation potential of the particular oxide involved. When these holdups are small, however, the starting potentials are not much different from the mid-point potential. Since the former can be measured more reproducibly, they are reported in Table I.

Several points should be noted in Table I. First, when the concentration of the redox system is too high, some of the steps are not observed on the potential-time curve. This does not indicate that the reactions are not occurring at the electrode but rather the rate of the reaction is too fast for the relatively slow pen and ink recorder to follow.

TABLE I

STARTING POTENTIALS OF STEPS IN THE POTENTIAL-TIME CURVES OF A GOLD ELECTRODE IMMERSED IN VARIOUS REDOX SYSTEMS

Redox system	*Starting potential*			
In 1N sulfuric acid	*Step B*	*Step C*	*Step D*	*Step E*
$4.7\times10^{-3}M$ Ce^{+4}/Ce^{+3}	—	—	—	+1.33
2.4×10^{-3}	—	—	—	+1.28
2.4×10^{-4}	+0.47	+0.72	—	+1.23
1.9×10^{-4}	+0.47	+0.71	+1.09	+1.22
9.5×10^{-5}	+0.45	+0.69	+1.06	+1.21
4.7×10^{-5}	+0.45	+0.66	+1.03	—
$2.8\times10^{-3}M$ MnO_4^-/Mn^{+2}	—	—	—	+1.30
2.8×10^{-4}	+0.45	+0.67	+1.09	+1.29
1.7×10^{-4}	+0.47	+0.67	+1.09	+1.27
1.1×10^{-4}	+0.47	+0.69	+1.05	+1.21
$2.3\times10^{-4}M$ $K_2Cr_2O_7$	+0.47	+0.69	+0.98	—
$2.6\times10^{-4}M$ $KBrO_3$	+0.47	+0.69	+0.98	—
In 0.1N sodium carbonate				
$2.2\times10\ ^{4}M$ MnO_4^-/Mn^{+2}	—0.29	+0.08	—	—

In the case of $4.7 \times 10^{-3} M$ Ce^{+4}/Ce^{+3}, the steps B, C, and D have been observed by replacing the recorder with an oscilloscope. Secondly, the number of steps which can be observed depends on the solution potential. Thus, in the case of dichromate and bromate as well as ceric at very low concentration, step E is absent. The slight shift of the starting potential with concentration parallels the effect of current density in electrolytic oxidation. Finally, the most important point in Table I is that the starting potentials are independent of the nature of the redox couple in the solution.

For comparison, Table II summarizes the starting potentials from electrolytic oxidations of the gold electrode along with the calculated potentials of the gold oxide/gold couples. The latter were calculated to the indicated pH values from the same data used by EL WAKKAD AND SHAM EL DIN[8]. It is clear from Table I and II that the starting potentials of the steps are independent of the method of oxidation, be it chemical or electrolytic. Furthermore, Steps B, D and E agree very well with the accepted potentials for the Au_2O/Au, AuO/Au and Au_2O_3/Au couples respectively. The reaction involved in step C, as has been pointed out previously, is the dissolution of the gold electrode.

TABLE II

STARTING POTENTIALS FOR ELECTRICAL OXIDATION OF GOLD IN VARIOUS MEDIA

Electrolyte	*Starting potential*				*Calculated potentials*		
	Step B	*Step C*	*Step D*	*Step E*	Au_2O/Au	AuO/Au	Au_2O_3/Au
1*N* Sulfuric acid (pH = 0)	+0.47	+0.73	+1.13	+1.33	+0.42	+1.04	+1.36
0.1*N* Sodium carbonate (pH = 11.2)	—0.25	+0.11	—	+0.63	—0.24	+0.38	+0.70

TABLE III

STARTING POTENTIALS OF CHEMICAL AND ELECTRICAL OXIDATION OF PLATINUM

Redox system	*Starting potential*	
In 1N sulfuric acid	*Step B*	*Step C*
$4.8 \times 10^{-3} M$ Ce^{+4}/Ce^{+3}	+0.90	—
1.9×10^{-3}	+0.80	—
9.4×10^{-4}	+0.81	+0.97
$5.6 \times 10^{-3} M$ MnO_4^-/Mn^{+2}	+0.87	—
2.7×10^{-3}	+0.82	—
2.7×10^{-4}	+0.71	+0.85
In 0.1N sodium carbonate		
$5.6 \times 10^{-4} M$ MnO_4^-/Mn^{+2}	—0.08	+0.30
Anodic current *In 1N sulfuric acid*		
240 microamps	+0.80	—
120	+0.77	—
60	+0.71	+0.87
30	+0.67	+0.86
In 0.1N sodium carbonate		
120 microamps	—0.01	+0.26
60	—0.05	+0.23
30	—0.03	+0.23

2. *Platinum electrode*

The potential-time curves obtained by the oxidations of the platinum electrode are not as well defined as those of the gold electrodes. They show an initial flat portion A, followed by a maximum of two changes of slope B and C, as seen in Fig. 4. The starting potentials are summarized in Table III along with the data obtained by electrolytic oxidation of the same electrode in the same background electrolyte. The variation in starting potential with concentration or current density is much more pronounced than in the case of gold.

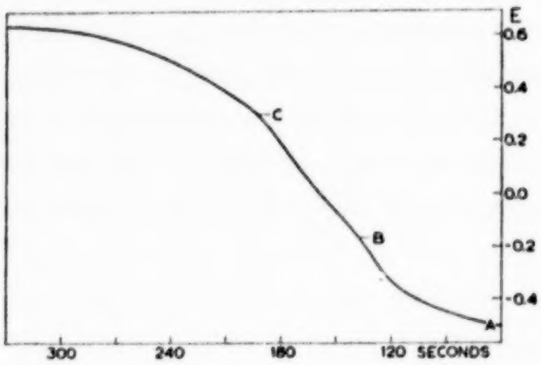

Fig. 4. Chemical oxidation of platinum electrode by permanganate in 0.1N sodium carbonate.

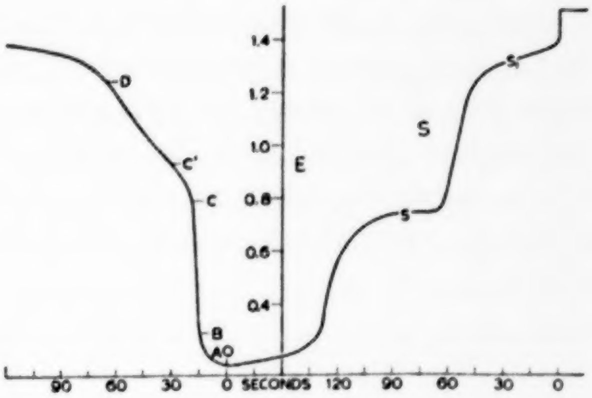

Fig. 5. Chemical oxidation of palladium electrode by permanganate in 1N sulfuric acid.

It has been well established that PtO is formed on a platinum surface during electrolytic oxidation. The potential of the PtO/Pt system from GRUBES' data is +0.88 V in 1N sulfuric acid and +0.22 in 0.1N sodium carbonate[10]. Step B on the potential-time curves seems to correspond to the formation of PtO at the electrode surface. Recently, EL WAKKAD AND EMARA showed that the formation of PtO_2 can also be observed in electrolytic oxidation when very low current density is employed. The present work confirms their result. It is shown in Table III that the step C can only be observed at the lowest concentration or current density. The step C seems to correspond to the formation of PtO_2. The calculated potential based on GRUBES' data for the PtO_2/Pt couple is +1.04 V in 1N sulfuric acid and +0.38 V in 0.1N sodium carbonate.

3. *Palladium electrodes*

Fig. 5 shows a typical potential-time curve for the chemical oxidation of palladium. The stripping pattern of the "oxidized" palladium electrode is also included. This pattern is independent of the nature of the oxidizing agent used. The flat portion S_1 and S_2 are attributed to the reduction of $Pd(OH)_4$ and $Pd(OH)_2$ respectively[9].

At the point o in Fig. 5, the cathodic current was turned off and the electrode was subjected to the chemical oxidation by the redox couple in the solution. After the initial flat portion A, the potential of the electrode begins to rise rapidly at B. The points of interest are C and D which represent the beginning of the formation of the two hydroxides.

The starting potentials of the chemical and the electrolytic oxidations agree quite well as can be seen in Table IV. They are, however, somewhat lower than the calculated potentials which are +0.91 and +1.55 V in 1N sulfuric acid. The potential holdups in the case of palladium are much more drawn out than those of the gold and platinum.

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It is understandable that the starting potential is lower than the mid-point potential which should correspond to the calculated potential. The mid-point of the relatively flat portion for step C in Fig. 5, *i.e.* C′, is +0.93. This value agrees very well with the calculated potential.

TABLE IV

STARTING POTENTIALS OF CHEMICAL AND ELECTRICAL OXIDATION OF PALLADIUM

Redox system In 1N sulfuric acid	*Starting potential*	
	Step C	*Step D*
$4.6 \times 10^{-3}M$ Ce^{+4}/Ce^{+3}	+0.74	+1.30
2.8×10^{-3}	+0.74	+1.28
$4.5 \times 10^{-3}M$ MnO_4^-/Mn^{+2}	+0.76	+1.29
2.2×10^{-3}	+0.76	+1.29
Anodic current In 1N sulfuric acid		
827 microamps	+0.77	+1.41
240	+0.75	+1.33

It was been pointed out by EL WAKKAD AND SHAM EL DIN that the $Pd(OH)_4$ is unstable and the evolution of oxygen at a palladium electrode depends on the formation of this hydroxide as an intermediate step[9]. The present work seems to confirm their finding. The potential-time curve obtained by the anodic oxidation of palladium in 1*N* sulfuric acid shows that the relatively stable potential at which oxygen is evolved is +1.55 V which is the calculated potential for the $Pd(OH)_4/Pd$ couple.

DISCUSSION

The magnitude of the holdups in the potential-time curves presented herein can be greatly magnified by employing electrodes with spongy surfaces, *i.e.*, platinum black, gold plated platinum etc. Compact metal electrodes are most frequently used in potentiometric measurements and hence only these were examined. Even under these conditions, the data shows that stepwise oxide formation occurs at the surfaces during the attainment of the solution potential. None of the indicating electrodes studied is truly inert in a strongly oxidizing aqueous solutions.

Due to the cathodic pretreatment of the electrode, there is some uncertainty as to the exact pH at the electrode solution interface. Furthermore, the rate of oxidation of the electrode, there is some uncertainty as to the exact pH at the electrode solution interface. Furthermore, the rate of oxidation of the electrode surface is a complex function of the diffusion of the chemical species, the electrode surface condition and many other variables. No theoretical treatment of the potential-time curve is attempted. While ROSS AND SHAIN[6], KOLTHOFF AND TANAKA[5] as well as other workers have already definitely shown that the "inert" electrodes are chemically oxidized, the present study shows the initial transient potential-time response. It is believed that this information might prove to be valuable in the understanding of the mechanism by which an indicating electrode acquired the solution potential.

ACKNOWLEDGEMENT

The authors are grateful to JOAN DICK and JEAN ANDERSON for their assistance in the preparation of the manuscript.

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SUMMARY

A comparison of the behavior of gold, platinum and palladium indicating electrodes in various strongly oxidizing solutions with the behavior observed when these electrodes are oxidized anodically reveals that the same reactions are occurring at the electrodes. These reactions are attributed to oxide (or hydroxide) film formation because the potentials at which these various reactions occur agree reasonably well with the potential of known oxide-metal transitions. The present study emphasizes the transient potential-time response of an indicating electrode when immersed in a strongly oxidizing solution. It is concluded that all "inert" indicating electrodes undergo stepwise chemical oxidation in strongly oxidizing media.

RÉSUMÉ

Une étude comparative entre le comportement des électrodes indicatrices d'or, de platine, et de palladium, dans différentes solutions fortement oxydantes et le comportement observé lorsque ces électrodes sont oxydées anodiquement a montré que les mêmes réactions se produisent aux électrodes. Ces réactions peuvent être attribuées à la formation d'un film d'oxyde ou d'hydroxyde, les potentiels auxquels se produisent ces différences réactions correspondant en effet bien au potentiel connu oxyde-métal. Cette étude fait ressortir la variation passagère du potentiel d'une électrode indicatrice avec le temps, lorsqu'elle est plongée dans une solution fortement oxydante. On arrive à la conclusion que toutes les électrodes indicatrices ,,inertes'' subissent une oxydation chimique graduelle dans un milieu fortement oxydant.

ZUSAMMENFASSUNG

Ein Vergleich des Verhaltens von Gold-, Platin- und Palladium- Indikatorelektroden in verschiedenen stark oxydierenden Lösungen mit dem Verhalten, das man beobachtet wenn diese Elektroden anodisch oxydiert werden, zeigt, dass dieselben Reaktionen an den Elektroden stattfinden. Diese Reaktionen werden der Bildung von Oxyd- oder Hydroxydfilmen zugeschrieben, weil die Potentiale bei denen diese verschiedenen Reaktionen stattfinden ziemlich gut mit den Potentialen von bekannten Oxyd-Metall-Übergängen übereinstimmen. Die vorliegende Arbeit betont die vorübergehende Potential-Zeit-Abhängigkeit einer Indikatorelektrode, wenn diese in eine stark oxydierende Lösung getaucht wird. Es wird geschlossen, dass alle ,,inerten'' Indikatorelektroden in stark oxydierenden Media eine stufenweise chemische Oxydation erleiden.

REFERENCES

[1] W. D. Bancroft, *Z. physik. Chem.*, 10 (1892) 387.
[2] J. A. V. Butler, *Trans. Faraday Soc.*, 19 (1924) 734.
[3] C. Friedenhagen, *Z. anorg. Chem.*, 29 (1902) 396.
[4] W. Nernst and A. Lessing, *Chem. Zentr.*, 2 (1902) 241.
[5] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, 26 (1954) 632.
[6] J. W. Ross and I. Shain, *Anal. Chem.*, 28 (1956) 548.
[7] S. E. S. El Wakkad and S. H. Emara, *J. Chem. Soc.*, (1952) 461.
[8] S. E. S. El Wakkad and A. M. Sham El Din, *J. Chem. Soc.*, (1954) 3098.
[9] S. E. S. El Wakkad and A. M. Sham El Din, *J. Chem. Soc.*, (1954) 3094.
[10] G. Grubes, *Z. Electrochem.*, 16 (1901) 621.

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VOLTAMMETRIC BEHAVIOR OF THE IRON(II)-(III) AND CERIUM(III)-(IV) COUPLES IN POTENTIOMETRIC TITRATIONS AT CONSTANT CURRENT AND AMPEROMETRIC TITRATIONS WITH TWO INDICATOR ELECTRODES

by

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INTRODUCTION

In recent years, several reviews have been given of the relations between voltammetry and potentiometric titrations at constant current and amperometric titrations[1,2,3,4], and expressions have been developed for the relations between current and potential in both reversible and incompletely reversible systems. In a review comparing experiment with theory, KOLTHOFF[5] has considered only either ideally reversible couples or completely electro-inactive (irreversible) couples. For potentiometric titrations at constant current using the platinum indicator electrode, the titration curve of the reversible copper(I)-(II) couple in ammoniacal medium with ethylene-diaminetetraacetate, which is not reducible at the platinum electrode, has been predicted quantitatively on the basis of the voltammetric behavior of the system titrated and the reagent[6]. In a similar manner, the titration curve of the reversible iodine-iodide couple with electro-inactive thiosulfate could be predicted quantitatively. For metals more electronegative than hydrogen, continuous electrodeposition on mercury in the form of an amalgam usually occurs reversibly, and mercury electrodes show great promise for potentiometric titrations at constant current of ions of metals less noble than copper. This has been substantiated in papers[7,8] published after the present work was terminated.

Many of the common oxidizing and reducing agents are not ideally reversible, and their potentials deviate from the reversible potentials, especially upon the passage of current at the electrode. We have observed that it is extremely difficult to closely reproduce the current-potential curves for incompletely reversible couples and that the shape of such curves greatly depends upon the pretreatment of the electrode. With incompletely reversible couples, it is possible to predict semiquantitatively, on the basis of voltammetric behavior but not of theoretical behavior, the titration curves in potentiometric titrations at constant current using one or two indicator electrodes and also in amperometric titrations. The method of amperometric titrations using two indicator electrodes was introduced by FOULK AND BAWDEN[9]; its relation to voltammetry has been considered by DELAHAY[10], and the amperometric nature of the end-point discussed thoroughly by BRADBURY[11] AND KOLTHOFF[5].

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In the present paper we have studied the voltammetric behavior of the iron(II)-(III) and cerium(III)-(IV) couples at rotated platinum electrodes in hydrochloric and sulfuric acid media. Based on this information, it has been possible to predict the shape of the titration curves for potentiometric titrations at constant current using one and two indicator electrodes and amperometric titrations using two indicator electrodes, and to consider the effects of e.m.f. and current upon the nature of the titration curves.

EXPERIMENTAL

C.P. chemicals and conductivity water were used to prepare all reagent solutions. Details have been described elsewhere[12].

Current-potential curves were recorded automatically using a Sargent model XXI polarograph wit a chart speed of 1 inch/minute and rates of change of potential of 0.074 and 0.148 volt/minute. Current-potential curves are not corrected for residual currents. A manual polarograph[12] was used (a) to apply a constant e.m.f. between the electrodes in amperometric titrations and (b) to maintain a constant current in potentiometric titrations. Current measurements were made with a Weston model 430 microammeter (0 to 30 μa) with an internal resistance of 158.6 ohms. No correction was made for the ohmic drop across the microammeter. Potential measurements were made with a Leeds and Northrup Students potentiometer. Potentials are referred to the saturated calomel electrode (S.C.E.). All measurements were made at 25.0 ± 0.1°C.

Platinum electrodes were prepared by sealing a short length of 18 gauge wire into the end of a 10 inch length of glass tubing. Electrical connection was made by filling the tube with mercury. The electrode was placed in a chuck and rotated with a synchronous motor about the axis of the tubing at 600 r.p.m. For titrations using two indicator electrodes, two concentric glass tubes were sealed at one end, and 14 gauge platinum wires were then sealed into the separate compartments of the electrode assembly[12]. The electrode in the outer compartment is rotated with a greater linear velocity than the inner electrode, and for electrodes of the same size, the outer electrode will exhibit a greater sensitivity. While this behavior is satisfactory, the two electrodes will not exhibit the same sensitivity unless the size of the outer electrode is reduced accordingly. The electrode sensitivity, k_{ion}, is defined as the magnitude of the limiting current observed for the given electrode reaction divided by the bulk concentration of the electroactive species. The electrodes used in this work exhibited sensitivities of 220 μa/mmole/l for the oxidation of iron(II) and 160 μa/mmole/l for the reduction of cerium(IV).

VOLTAMMETRIC BEHAVIOR OF THE IRON(II)-(III) AND CERIUM(III)-(IV) COUPLES AT A ROTATED PLATINUM ELECTRODE

The behavior of a platinum electrode in an inert electrolyte free from oxidizable or reducible matter has been discussed by HICKLING[13] and KOLTHOFF AND TANAKA[14]. In 1M sulfuric acid, the surface of the electrode is oxidized at potentials more positive than about +0.8 V *vs.* S.C.E., and the resulting platinum(II) oxide is reduced at potentials less than +0.7 V. A film is also formed with appropriate oxidizing agents, *e.g.* cerium(IV), and it is reduced by appropriate reducing agents, *e.g.* iron(II). Fig. 1 compares the current-potential curves observed at a clean platinum electrode free from oxide film with those calculated assuming a reversible couple for solutions containing 1M sulfuric acid, 0.05M ferric sulfate, and varying concentrations of ferrous sulfate. Each curve was recorded automatically starting from +0.75 V to more negative potentials with a rate of change of potential of —0.074 V/min. It is apparent that the current-potential curves do not represent a reversible electrode reaction. For the oxidation of iron(II), limiting currents are not obtained, and the slope of the curves about the null potentials are much less than predicted on the basis of reversibility. Fig. 2 compares the calculated and experimental current-potential curves for the same solutions as in Fig. 1 at a platinum electrode, the surface of which had been oxidized with cerium(IV) prior to electrolysis. The curves were recorded automatically starting at +1.10 V with a rate of change of potential of —0.074 V/min. In comparison with Fig. 1, the curves in Fig. 2

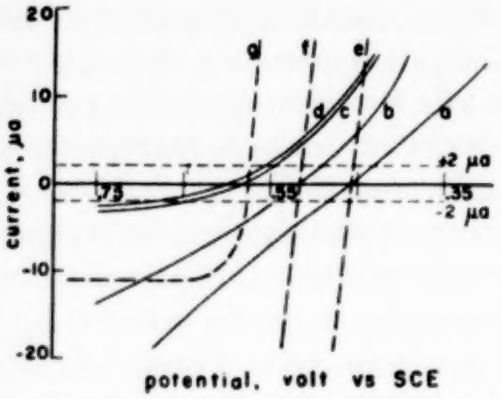

Fig. 1. Comparison of experimental and calculated current-potential curves at clean platinum electrode, $k_{Fe(II)}$ = 220 μa/mmole/l. 1M sulfuric acid and 0.05M iron(III). Experimental curves: (a) 5.0 × $10^{-3}M$ iron(II); (b) 5.0 × $10^{-4}M$; (c) 5.0 × $10^{-5}M$; (d) iron(II) = 0. Calculated curves: (e) 5.0 × $10^{-4}M$ iron(II); (f) 5.0 × $10^{-4}M$; (g) 5.0 × $10^{-5}M$.

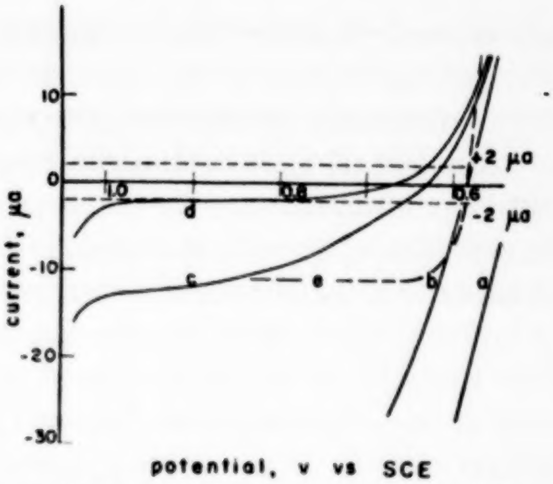

Fig. 2. Same as in Fig. 1, but at "oxidized" platinum electrode. Curves (a) to (d) same as in Fig. 1. Calculated curve (e) 5.0 × $10^{-5}M$ iron(II).

show fairly well-defined limiting current regions for the more dilute iron(II) solutions, and exhibit larger slopes about the null potentials approaching those of reversible electrode reactions as the ferrous iron concentration increases. The observation that an oxide film increases the reversibility of the reaction is well supported by the studies of LAITINEN AND KOLTHOFF[15], LORD AND ROGERS[16], and MÜLLER[17], all of whom have reported that "pre-anodizing" the electrode or "starting the polarograph at a very positive potential" increases the reversibility of the couple under consideration.

Insight into the behavior of the oxidized platinum electrode is offered by current-time curves; Fig. 3 shows current-time curves recorded automatically for the reduction of iron(III) at constant potential at an oxidized platinum electrode in a solution containing 0.05M ferric and 0.0005M ferrous sulfate in 1M sulfuric acid. As the oxidized electrode is immersed into the solution, the oxide film is reduced, primarily electrochemically, and initially the reduction current is large. The current decreases with time as the film is

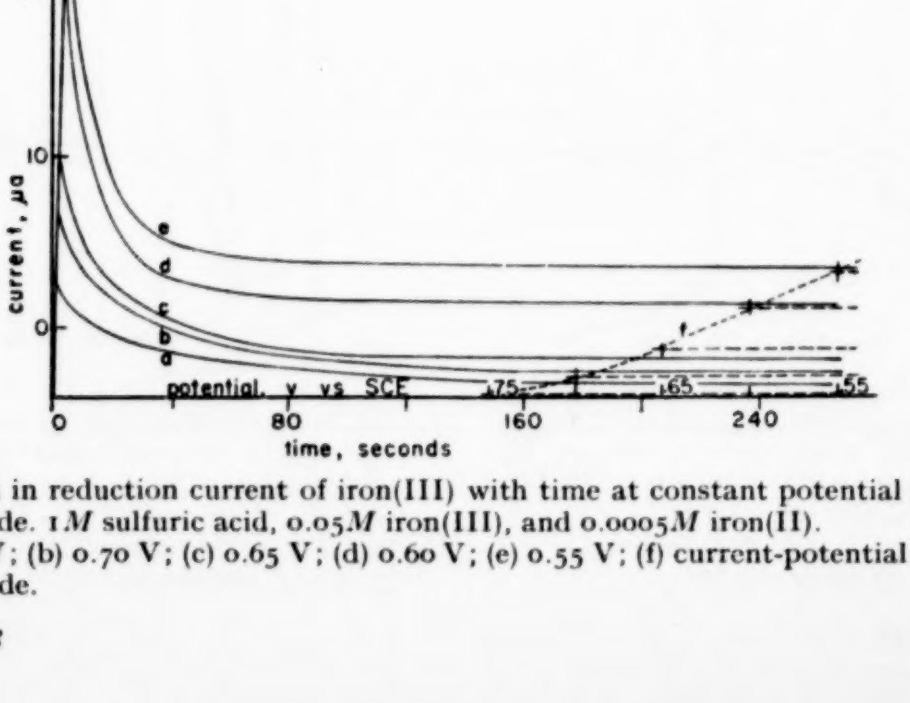

Fig. 3. Variation in reduction current of iron(III) with time at constant potential at "oxidized" platinum electrode. 1M sulfuric acid, 0.05M iron(III), and 0.0005M iron(II).
(a) E = +0.75 V; (b) 0.70 V; (c) 0.65 V; (d) 0.60 V; (e) 0.55 V; (f) current-potential curve at *clean* platinum electrode.

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reduced, and when the film is completely removed, the current reaches a steady limiting value corresponding to the value in the current-potential curve at a clean electrode. Curve f compares the current-potential curve at a clean electrode (cathodic portion of curve c in Fig. 1) with the limiting currents obtained at the various potentials. At more positive potentials (curves a and b), the film disappears more slowly than at more negative potentials (curves c, d, and e). If the electrode is not rotated but remains stationary, the rate of electrochemical reduction is decreased, and the deviation in current from the limiting value persists over longer periods of time. The greater ease of reduction of the iron(III) at the oxide coated electrode may be attributed to a bridge formation between the oxygen of the film and the hydrated iron(III) ion, thus facilitating the electron transfer between the electrode and the ion[18].

The iron(II)-(III) couple is more nearly reversible in hydrochloric acid than in sulfuric acid. Fig. 4 presents current-potential curves observed for solutions containing 1 M hydrochloric acid, 0.05 M ferric sulfate, and varying concentrations of ferrous sulfate. The curves exhibit large slopes about the null potentials approaching those of reversible. reactions, and the limiting currents are well-defined. In hydrochloric acid media, an oxide film is not formed on the surface of the electrode. The presence of chloride ions

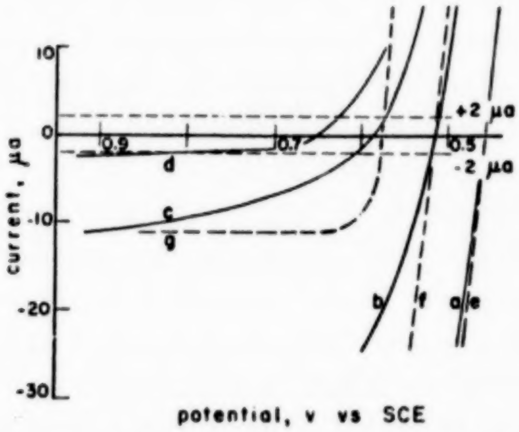

Fig. 4. Current-potential curves in 1 M hydrochloric acid and 0.05 M iron (III) $k_{Fe(II)}$ 220 µa/mmole/l. Experimental curves: (a) $5.0 \times 10^{-3} M$ iron(II); (b) $5.0 \times 10^{-4} M$; (c) $5.0 \times 10^{-5} M$; (d) iron(II) = 0. Calculated curves: (e) $5.0 \times 10^{-3} M$ iron(II); (f) $5.0 \times 10^{-4} M$; (g) $5.0 \times 10^{-5} M$.

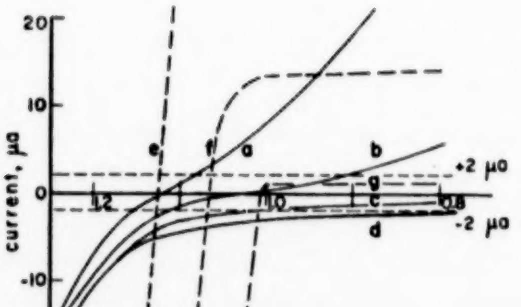

Fig. 5. Current-potential curves in 1 M sulfuric acid and 0.05 M cerium(III). $k_{Ce(IV)}$ 160 µa/mmole/l. Experimental curves: (a) $1.0 \times 10^{-3} M$ cerium(IV); (b) $1.0 \times 10^{-4} M$; (c) $1.0 \times 10^{-5} M$; (d) cerium(IV) = 0. Calculated curves: (e) $1.0 \times 10^{-3} M$ cerium(IV); (f) $1.0 \times 10^{-4} M$; (g) $1.0 \times 10^{-5} M$.

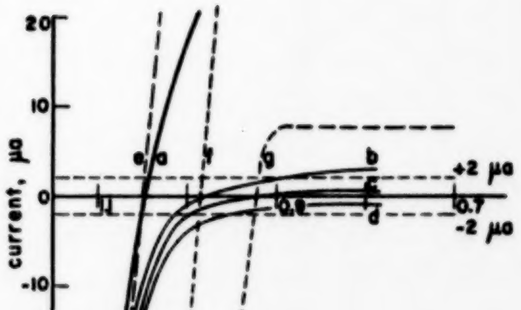

Fig. 6. Same as in Fig. 5, but in 1 M hydrochloric acid. Experimental curves: (a) $5.0 \times 10^{-3} M$ cerium(IV); (b) $5.0 \times 10^{-4} M$; (c) $5.0 \times 10^{-5} M$; (d) cerium(IV) = 0. Calculated curves: (e) $5.0 \times 10^{-3} M$ cerium(IV); (f) $5.0 \times 10^{-4} M$; (g) $5.0 \times 10^{-5} M$

in the coordination sphere of an iron ion apparently increases the ease of electron transfer to and from the iron species.

Figs. 5 and 6 compare with the calculated curves the experimental current-potential curves observed at an electrode with sensitivity of 160 μa/mmole/l for solutions containing 0.05M cerous sulfate and varying concentrations of ceric sulfate in 1M sulfuric acid and 1M hydrochloric acid respectively. The cerium couple is highly irreversible in sulfuric acid even though the electrode is coated with an oxide film. In hydrochloric acid medium, the system is less irreversible than in sulfuric acid.

POTENTIOMETRIC TITRATIONS AT CONSTANT CURRENT

A. Use of one indicator electrode and reference electrodes

From the curves in Figs. 1, 4, 5, and 6 it is possible to predict the curves for potentiometric titrations at constant current of iron(II) with cerium(IV) in sulfuric and hydrochloric acid media using both one and two indicator electrodes. Consider for example, the titration of 0.1M iron(II) with 0.1M cerium(IV) in 1M sulfuric acid at a current of +2 μa using one indicator electrode, with sensitivity for iron(II) of 220 μa/mmol e/l, and an external reference electrode (S.C.E.). When 91% of the initial iron(II) has been oxidized, iron(II) = 0.005M and iron(III) is approximately 0.05M, and the potential of the electrode will be that in curve a of Fig. 1 at which the current is equal to +2 μa, +0.44 v. AT 99.9% when iron(II) = 0.00005M, the potential will have shifted to the corresponding point on curve c in Fig. 1, +0.54 v. After the equivalence point, the potential will be determined by the cerium(III)-(IV) couple. At 100.1%, cerium(III) = 0.05M and cerium(IV) = 0.00005M, and from curve c in Fig. 5, the potential is approximately +0.77 v.

In Fig. 7, experimental and calculated curves are compared with those predicted from the current-potential curves in Figs. 1 and 5 for the titration of 0.1M iron(II) with

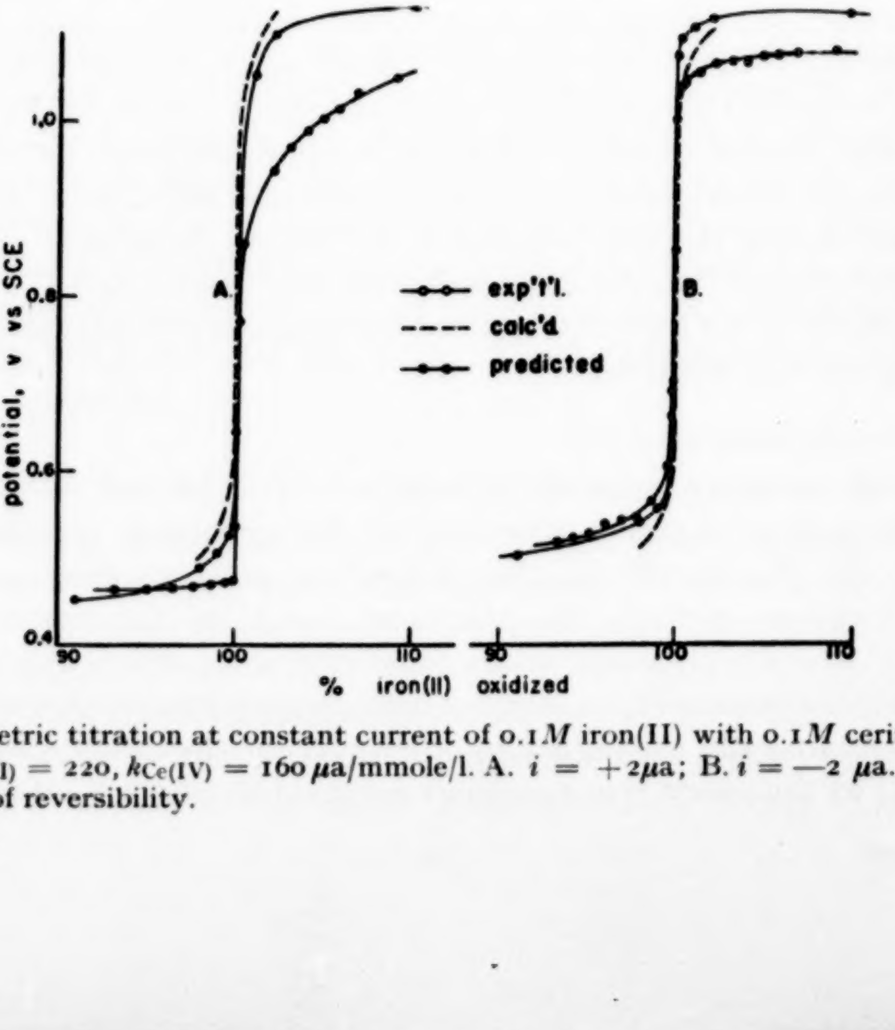

Fig. 7. Potentiometric titration at constant current of 0.1M iron(II) with 0.1M cerium(IV) in 1M sulfuric acid. $k_{Fe(II)} = 220$, $k_{Ce(IV)} = 160$ μa/mmole/l. A. $i = +2$μa; B. $i = -2$ μa. "Calculated" curve is on basis of reversibility.

0.1*M* cerium(IV) in 1*M* sulfuric acid at +2 and —2 μa. When titrating at a constant anodic current (—2 μa), the potentials are more positive than the corresponding zero current potentials. With the indicator electrode of given sensitivity, the end-point calculated assuming reversible couples[5,10] is 0.02% early. When titrating at a constant cathodic current (+2 μa), the potentials are more negative than the corresponding zero current potentials and the calculated end-point is 0.025% late. These deviations from the equivalence point are too small to be detected experimentally, but with more dilute solutions[5,10], the errors become appreciable.

The error in the titration increases linearly with increasing current at a given dilution and with increasing dilution at constant current. The increase in error with decreasing concentrations of reagents at a given sensitivity is illustrated by Fig. 8 in which are compared the experimental and calculated curves for the titrations of 0.002*M* iron(II) with 0.002*M* cerium(IV) in 1*M* hydrochloric acid. For identical electrodes with the indicated sensitivity, the theorectical error increases for 0.1*M* solutions from —0.02% to —0.9% for 0.002*M* solutions at constant anodic current of —2 μa, while the corresponding values at constant cathodic current of +2 μa are +0.025% and +1.2%. The experimental errors for the 0.002*M* solutions were about —3.5% at —2 μa and +3.5% at +2 μa. While chloride ions are oxidized at an appreciable rate by 0.1*M* cerium(IV) solutions[19], the rate of oxidation for 0.002*M* solutions is sufficiently slow as to cause negligible error during the time required for a titration. In sulfuric acid, the slopes of the current-potential curves about the null potentials (Figs. 1 and 5) are so small that the titration curves do not show any appreciable change in potential near the equivalence point using 0.002*M* solutions.

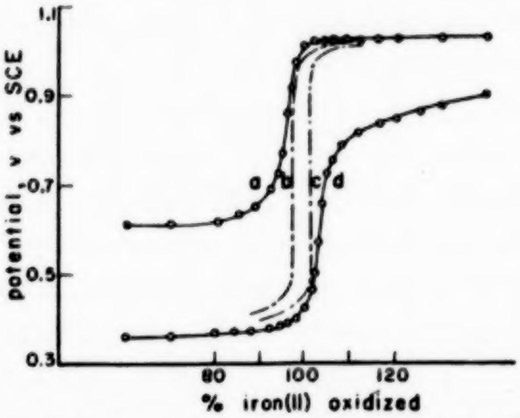

Fig. 8. Potentiometric titration at constant current of 0.002*M* iron(II) with 0.002*M* cerium(IV) in 1*M* hydrochloric acid. $k_{\mathrm{Fe(II)}}$ 220, $k_{\mathrm{Ce(IV)}}$ 160 μa/mmole/l. (a) $i = -2$ μa, experimental; (b) $i = -2$ μa, calculated on basis of reversibility; (c) $i = +2$ μa, calculated; (d) $i = +2$ μa, experimental.

B. Use of two indicator electrodes

If the external reference electrode is replaced by a second indicator electrode, the electrode system becomes identical to the polarized monometallic system of WILLARD AND FENWICK[20] or the derivative polarographic one of FURMAN *et al.*[4]. At constant current, the maximum e.m.f. in the titration of iron(II) with cerium(IV) occurs at or near the equivalence point where there is practically neither iron(II) nor cerium(IV) in solution, and a large potential difference is required to permit simultaneously the reduction of iron(III) at the cathode and the oxidation of cerium(III) at the anode. For titrations using 0.1*M* solutions, the e.m.f. required

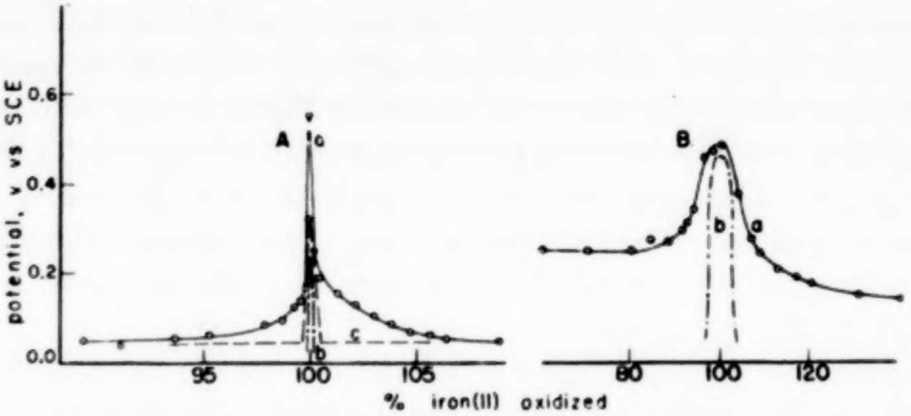

Fig. 9. Potentiometric titration at constant current of 2 μa using two indicator electrodes ($k_{Fe(II)}$ = 220, $k_{Ce(IV)}$ = 160 μa/mmole/l) of iron(II) with cerium (IV).
A. 0.1*M* solutions in 1*M* sulfuric acid: (a) experimental; (b) calculated on basis of reversibility; (c) predicted from current-potential curves.
B. 0.002*M* solutions in 1*M* hydrochloric acid: (a) experimental; (b) calculated.

to support a current of 2 μa may be predicted from the difference in potentials of the anode and cathode in Figs. 1 and 5 or from Fig. 7. In Fig. 9 the experimental curves are compared with those calculated theoretically and with those predicted from the current-potential curves for the titration at 2 μa of 0.1*M* iron(II) with 0.1*M* cerium(IV) in 1*M* sulfuric acid using two indicator electrodes of given sensitivity; a similar comparison between the experimental and calculated curves is presented in Fig. 9 for the titration using 0.002*M* solutions in 1*M* hydrochloric acid. For 0.1*M* solutions, both the predicted and experimental end-points are less acute than the theoretical; the maximum in e.m.f. is sufficiently large to permit determination of an accurate end-point. For titrations using 0.002*M* solutions in 1*M* hydrochloric acid, the theoretical e.m.f. increases from near zero at 97% to greater than 0.4 v at 99%, remains approximately constant until 101%, and then decreases to almost zero at 103%; the experimental curve exhibits a much broader maximum and is not sufficiently accurate for a practical end-point.

Characteristic of these methods, the accuracy of a potentiometric titration at constant current using one or two indicator electrodes may be increased by increasing the size of the electrode or decreasing the magnitude of the titration current. While it is not feasible to reduce the titration current to much less than 1 μa, the electrode size may be easily increased 10 or 15 times over that used in this work. For the titration of 0.002*M* solutions of iron(II) with cerium(IV) in 1*M* hydrochloric acid using two indicator electrodes, the range over which the maximum in e.m.f. is approximately constant is 2% for electrodes with sensitivity of 100 μa/mmole/l and 0.2% for a sensitivity of 1000 μa/mmole/l.

AMPEROMETRIC TITRATIONS USING TWO INDICATOR ELECTRODES

In a manner similar to that for potentiometric titrations, it is possible to predict the titration line for an amperometric titration using two inert electrodes from the current-potential curves for the system. Consider the titration of 0.1*M* iron(II) with 0.1*M* cerium(IV) in 1*M* sulfuric acid with a constant e.m.f. of 100 mV applied between two indicator electrodes of stated sensitivity. When 91% of the initial iron(II) has been oxidized, iron(II) = 0.005*M* and iron(III) is approximately 0.05*M*. From curve a in Fig. 1 in which the zero-current potential is approximately +0.47 V, and e.m.f. of

100 mV will allow in such a solution a current of about 4 μa to flow. The potential of the anode will be about +0.42 V, and that of the cathode, +0.52 V. At 99.9%, iron(II) is 0.00005*M*, and from curve c in Fig. 1, a current of about 1.1 μa will flow; the anode potential is +0.65 V, the zero-current potential is +0.58 V, and the cathode potential is +0.55. $(\pi_a - \pi_o) = 0.07$ V, and $(\pi_o - \pi_c) = 0.03$ V where π_a, π_o and π_c are the anode, zero-current, and cathode potentials respectively. In a similar manner, the current after the end-point may be predicted from the current-potential curves for the cerium-(III)-(IV) couple in Fig. 5.

Fig. 10 compares the experimental curves and the curves calculated for reversible reactions[5,11,12] for amperometric titrations using two indicator electrodes with indicated sensitivity for the titration of 0.002*M* iron(II) with 0.002*M* cerium(IV) in 1*M* sulfuric acid. A similar comparison for titrations in 1*M* hydrochloric acid is presented in Fig. 11.

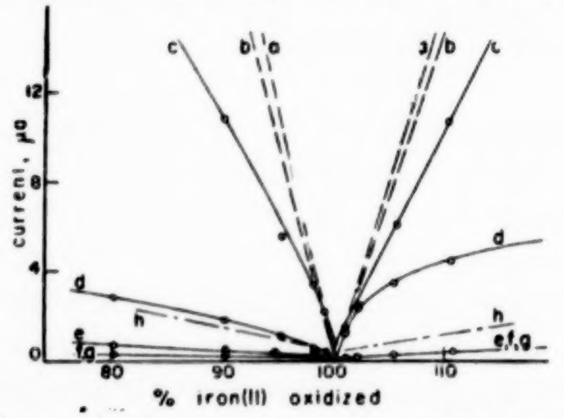

Fig. 10. Amperometric titration using two indicator electrodes ($k_{\mathrm{Fe(II)}} = 220$, $k_{\mathrm{Ce(IV)}} = 160$ μa/mmole/l) of 0.002*M* iron(II) with 0.002*M* cerium(IV) in 1*M* sulfuric acid. Calculated lines on basis of reversibility: (a) e.m.f. = 500 and 200 mV; (b) 100 mV. Experimental: (c) e.m.f. = 500 mV; (d) 200 mV; (e) 100 mV; (f) 50 mV; (g) 20 mV. Predicted: (h) e.m.f. = 100 mV.

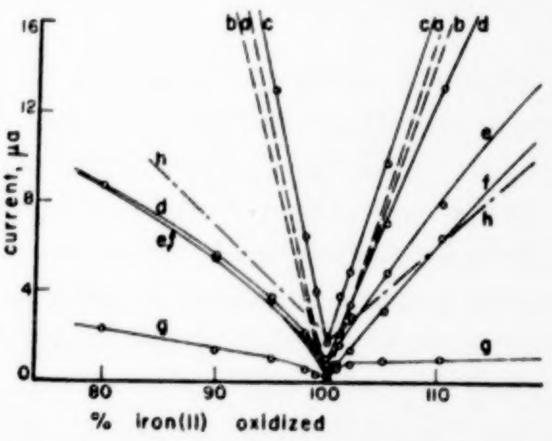

Fig. 11. Same as in Fig. 10 for amperometric titration but in 1*M* hydrochloric acid. Calculated lines: (a) e.m.f. = 500 and 200 mV; (b) 100 mV. Experimental: (c) e.m.f. = 500 mV; (d) 200 mV; (e) 100 mV; (f) 50 mV; (g) 20 mV. Predicted: (h) e.m.f. = 100 mV.

In hydrochloric acid medium the iron and cerium couples are less irreversible than in sulfuric acid and the titration lines are closer to those calculated on the basis of reversibility. In hydrochloric acid the experimental curve e in Fig. 11 for an e.m.f. of 100 mV compares favorably with curve h predicted from the current-potential curves; in Fig. 10, similar agreement is not obtained between the experimental curve e and the predicted curve h for an e.m.f. of 100 mV in sulfuric acid medium.

Curve a in Fig. 12 illustrates the titration curve of 0.002*M* iron(II) with 0.002*M* cerium(IV) in 1*M* sulfuric acid at an applied e.m.f. of 100 mV. As has been discussed already, the slope of the lines are very much smaller than those calculated on the basis of reversibility. It is interesting to note that curve b in Fig. 12, representing the titration of 0.002*M* cerium(IV) with 0.002*M* iron(II) in 1*M* sulfuric acid at an applied e.m.f. of 100 mv, gives a much steeper line as excess reagent is added beyond the equivalence point than in the reverse titration. The reason is that in cerium(IV) solutions the electrode becomes covered with an oxide film which is only slowly removed after the end-point. In the presence of this film, the iron couple is much less irreversible than at a clean electrode (Fig. 2), and therefore the titration line for the excess iron(II) reagent is much steeper than the corresponding line for the excess cerium(IV) reagent at the clean electrode.

As has been discussed before, the anode and cathode potentials differ from the zero-current potential when current passes in the system. Assuming reversible electrode reactions, it is possible to calculate the differences between the anode and cathode potentials and the zero-current potentials as a function of the applied e.m.f., independent of the electroactive species or electrode sensitivity[5,11,12]. For one-electron reactions, these calculated differences are listed in Table I as a function of the applied e.m.f. The experimental data in Table I are the average values measured in the vicinity of the end-points for the titrations of 0.002 *M* iron(II) with 0.002 *M* cerium(IV) in 1 *M* hydrochloric acid for e.m.f.'s of 100 and 500 mV. Both the anode and cathode potentials are more negative than the values calculated on the basis of reversibility. The difference between the theoretical and experimental values is a qualitative measure of the degree of irreversibility of the electrode reactions.

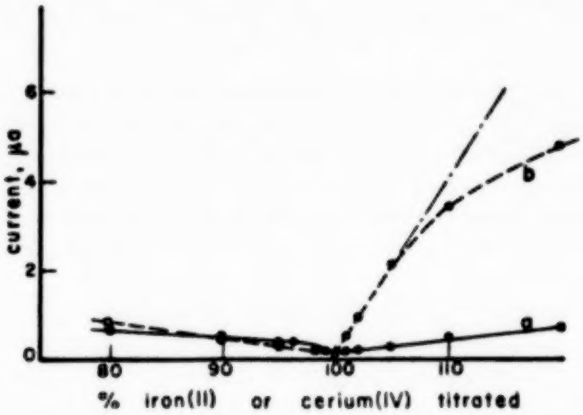

Fig. 12. Amperometric titration using two indicator electrodes ($k_{Fe(II)}$ = 220, $k_{Ce(IV)}$ = 160 μa/mmole/l). e.m.f. = 100 mV. (a) 0.002 *M* iron(II) titrated with 0.002 *M* cerium(IV); (b) 0.002 *M* cerium(IV) titrated with 0.002 *M* iron(II).

TABLE I

DIFFERENCES, IN VICINITY OF THE END-POINT, BETWEEN ANODE OR CATHODE POTENTIALS AND ZERO-CURRENT POTENTIALS AS A FUNCTION OF APPLIED e.m.f. IN TITRATION OF 0.002 *M* IRON(II) WITH 0.002 *M* CERIUM(IV) IN 1 *M* HCl

E.m.f., mV	$(\pi_0-\pi_a)$, *mV* *calc.*	$(\pi_0-\pi_a)$, *mV* *exptl.*	$(\pi_0-\pi_c)$, *mV* *calc.*	$(\pi_0-\pi_c)$, *mV* *exptl.*
10	− 5.5		+ 4.5	
20	− 12.0		+ 8.0	
50	− 36.0		+ 14.0	
100	− 83	−48 iron(II)-(III) −36 cerium(III)-(IV)[a]	+ 13.0	+ 50 iron(II)-(III) + 62 cerium(III)-(IV)[b]
200	−182	—	+ 18.0	
500	−482	−410 iron(II)-(III) −428 cerium(III)-(IV)[a]	+ 18.0	+ 90 iron(II)-(III) + 72 cerium(III)-(IV)[b]
1000	−982		+ 18.0	

[a] $(\pi_0-\pi_c)$ for cerium (III)-(IV)
[b] $(\pi_0-\pi_a)$ for cerium(III)-(IV)

SUMMARY

The voltammetric behavior at the rotated platinum electrode of the iron(II)-(III) and cerium(III)-(IV) couples in sulfuric and hydrochloric acids has been investigated. The iron and cerium couples are not reversible at a platinum electrode when current flows in the system, and the current-potential curves deviate considerably from those predicted on the basis of reversibility. Titration curves for potentiometric titrations at constant current using one and two indicator electrodes are predicted from the current-potential curves and compared with the experimental curves.

The degree of reversibility of the iron couple depends greatly on the pretreatment of the electrode. The current-potential curves of the iron couple at a platinum electrode coated with a monomolecular film of platinum oxide approach reversibility while those at a clean electrode are highly irreversible. Experimental and calculated titration lines for amperometric titrations using two indicator electrodes are compared, and the effects of medium and applied e.m.f. upon the characteristics of the titration curves are considered.

RÉSUMÉ

Les auteurs ont étudié le comportement voltammétrique à l'électrode rotative de platine des couples fer(II)-(III) et cérium (III)-(IV) dans les acides sulfurique et chlorhydrique. Les couples fer et cérium ne sont pas réversibles à l'électrode de platine lorsqu'on fait passer le courant dans le système; les courbes courant-potentiel diffèrent considérablement de celles prévues lorsqu'il y a réversibilité. Les courbes des titrages potentiométriques à courant constant, utilisant une et deux électrodes indicatrices, sont établies à partir des courbes courant-potentiel et comparées avec les courbes expérimentales.

Le degré de réversibilité du couple du fer dépend beaucoup du traitement préalable de l'électrode. Les courbes courant-potentiel du couple fer(II)-(III) à une électrode de platine, recouverte d'un film monomoléculaire d'oxyde de platine, s'approchent de la réversibilité, tandis que celles obtenues avec une électrode de platine pur sont irréversibles. Les courbes expérimentales et calculées pour les titrages ampérométriques utilisant deux électrodes indicatrices sont comparées; les effets du milieu et de la force électromotrice appliquée sur les caractéristiques des courbes de titrage sont examinées.

ZUSAMMENFASSUNG

Das voltammetrische Verhalten an der rotierenden Platinelektrode der Eisen(II)-(III) und Cer(III)-(IV)-Paare in Schwefel- und Salzsäure wurde untersucht. Die Eisen- und Cerpaare sind an einer Platinelektrode nicht reversibel wenn ein Strom durch das System geht und die Strom-Spannungs-Kurven weichen merklich von den auf Grund der Reversibilität zu erwartenden ab. Titrationskurven für potentiometrische Titrationen mit konstantem Strom und mit einer und zwei Indikatorelektroden wurden auf Grund der Strom-Spannungs-Kurven vorausgesagt und mit den experimentellen Kurven verglichen.

Die Reversibilität des Eisenpaares hängt hauptsächlich von der Vorbehandlung der Elektrode ab. Die Strom-Spannungs-Kurven des Eisenpaares an einer mit einem monomolekularen Platinoxydfilm überzogenen Platinelektrode sind nahezu reversibel, während diejenigen an einer reinen Elektrode höchst irreversibel sind. Experimentelle und berechnete Titrationskurven für amperometrische Titrationen mit zwei Indikatorelektroden werden verglichen und die Wirkungen von Medium und angewendeter EMK auf die Eigentümlichkeiten der Titrationskurven besprochen.

REFERENCES

[1] G. Duyckaerts, *Ind. chim. belge*, 18 (1935) 795.
[2] G. Charlot and D. Bézier, *Méthodes Électrochimiques d'Analyse*, Masson et Cie., Paris, 1954.
[3] N, H. Furman, *Anal. Chem.*, 26 (1954) 84.
[4] C. N. Reilley, W. D. Cooke and N. H. Furman, *Anal. Chem.*, 23 (1951) 1223.
[5] I. M. Kolthoff, *Anal. Chem.*, 26 (1954) 1685.
[6] I. M. Kolthoff and E. R. Nightingale, Jr., unpublished work.
[7] R. N. Adams, *Anal. Chem.*, 26 (1954) 1933.
[8] N. Tanaka, I. T. Oiwa and M. Kodama, *Anal. Chem.*, 28 (1956) 1555.
[9] C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, 48 (1926) 2045.
[10] P. Delahay, *Anal. Chim. Acta*, 4 (1950) 635.
[11] J. H. Bradbury, *Trans. Faraday Soc.*, 49 (1953) 304; 50 (1954) 959.
[12] E. R. Nightingale, Jr., *Ph. D. Thesis*, University of Minnesota, 1955.
[13] A. Hickling, *Trans. Faraday Soc.*, 41 (1945) 333.
[14] I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, 26 (1954) 632.
[15] H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, 45 (1941) 1063, 1074.
[16] S. S. Lord and L. B. Rogers, *Anal. Chem.*, 26 (1954) 284.
[17] O. H. Müller, *Science*, 109 (1949) 61.
[18] H. Taube and H. Myers, *J. Am. Chem. Soc.*, 76 (1954) 2103.
[19] F. R. Duke and C. E. Borchers, *J. Am. Chem. Soc.*, 75 (1954) 5186.
[20] H. H. Willard and F. Fenwick, *J. Am. Chem. Soc.*, 44 (1922) 2205, 2216.

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DÉTERMINATION DES CONSTANTES DE STABILITÉ DES COMPLEXES DE Tl^+ AVEC L'ACIDE ÉTHYLÈNEDIAMINOTÉTRACÉTIQUE (EDTA) ET AVEC L'ACIDE NITRILOTRIACÉTIQUE (NTA)

par

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Depuis quelques années le dosage polarographique du thallium est devenu très important en toxicologie. Cependant, la vague cathodique des ions Pb^{+2}, qu'on trouve ordinairement en petites quantités dans l'organisme, n'est pas suffisamment séparée de celle des ions Tl^+ pour permettre des conclusions sûres.

D'autres ions, tels que Cu^{+2}, réduits à l'électrode à un potentiel plus positif que les ions Tl^+, gêneront également quand ils sont présents en grandes quantités.

Par l'addition d'un complexant le potentiel demi-onde de l'ion complexé est déplacé vers des valeurs plus négatives, le déplacement étant fonction de la concentration du complexant et de la constante de stabilité du complexe formé.

Les constantes des complexes de l'EDTA et d'autres réactifs du même groupe avec plusieurs cations ont été déterminées e.a. par SCHWARZENBACH *et al.*[1], KORYTA ET KOSSLER[2], GOFFART, MICHEL ET DUYCKAERTS[3].

PŘIBIL ET ZABRANSKY[4] ont déterminé le thallium en présence de Pb^{+2} et de Cu^{+2} en complexant ces derniers par l'EDTA. Dans une solution de pH<4 le Tl^+ ne formerait pas de complexe.

HEYNDRICKX ET COLLAER[5] mentionnent également que Tl^+ ne forme pas de complexe avec EDTA en milieu acide.

A notre connaissance les constantes de stabilité des complexes de Tl^+ avec EDTA et avec NTA n'ont pas été déterminées. Nous nous sommes proposés de les calculer à partir du déplacement du potentiel demi-onde en fonction de la concentration du complexant, et de déterminer la stabilité des complexes formés en fonction du pH.

Appareillage

Les polarogrammes ont été enregistrés au polarographe Heyrowsky et Shikata, dont le galvanomètre et le tambour photographique ont été remplacés par un potentiomètre enregistreur Honeywell-Brown. La sensibilité de l'appareil était de $1.25 \cdot 10^{-8}$ A par division de l'échelle, et était réglable au moyen d'un potentiomètre. La linéarité de l'échelle fut contrôlée pour différentes sensibilités au moyen d'une source constante et d'une boîte de résistances étalons. Les mesures précises du courant limite de diffusion et du potentiel demi-onde ont été faites par opération manuelle.

La cellule d'électrolyse est représentée dans la Fig. 1. Elle a un volume total de 50 ml et est pourvue d'une circulation d'eau thermostatisée. Toutes les mesures ont été faites à $25° \pm 0.1°$C.

Nous avons employé un capillaire Tinsley, longueur 80 mm, diamètre intérieur 0.025 mm.

Le même capillaire a été employé dans tous les essais. La pression du mercure fut réglée de façon à obtenir une goutte en 3.8 sec.

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Les pH des différentes solutions ont été mesurés au pH-mètre Radiometer type 3, étalonné au moyen d'une solution de biphtalate de potassium 0.05*M*, de pH 4.00.

L'électrode de référence était une électrode au calomel saturée, reliée à la solution à mesurer par l'intermédiaire d'un pont de jonction suivant HUME ET HARRIS[6].

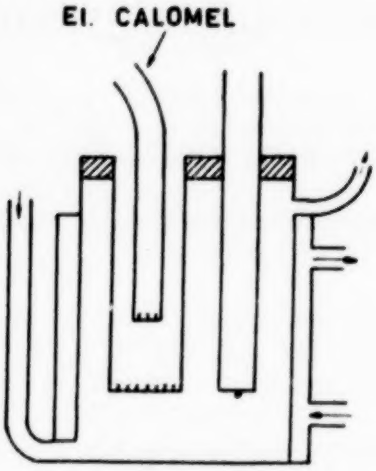

Fig. 1.

Solutions

Deux solutions stock de Tl⁺ $2.10^{-3}N$ ont été préparées: une solution de Tl_2SO_4, produit Riedel de Häen p.a., employé pour l'étude du complexe Tl⁺ + EDTA, et une solution de TlCl, produit Poulenc p.a., pour l'étude du complexe Tl⁺ + NTA. Les différentes solutions mesurées ont été obtenues par dilution de cette solution stock.

K_2SO_4 et KCl ont été employés comme électrolyte indifférent. Des solutions respectivement 0.4*N* et 2*N* ont été préparées au moyen des produits Merck p.a.

Une solution tampon, préparée au moyen de phosphate monopotassique 0.1*M*, et une solution d'hydroxyde de potassium 0.1*M*, ont été employées pour réaliser les différents pH désirés.

Une solution de gélatine à 1%, produit Hopkins et Williams, a été employée pour supprimer les maxima. La solution stock est conservée à 0°C.

Les solutions de concentration déterminée en EDTA et en NTA sont préparées par pesée directe de la quantité nécessaire et mise en solution dans une quantité adéquate de la solution de Tl⁺ et d'électrolyte indifférent.

Pour la préparation de toutes les solutions, on a uniquement employé l'eau bidistillée.

Conditions générales

La quantité désirée de EDTA, ou de NTA, produits Merck, est pesée directement dans un ballon jaugé de 100 ml. On ajoute 10 ml de la solution de Tl⁺ de concentration souhaitée, et 50 ml de la solution de l'électrolyte indifférent, et, dans le cas du complexe avec NTA, 10 ml de la solution de phosphate. On neutralise partiellement en ajoutant lentement une solution d'hydroxyde de potassium 0.1*N*, jusqu'à obtenir approximativement le pH désiré, et on remplit jusqu'au trait avec l'eau bidistillée. Le pH exact de la solution obtenue est déterminé au pH-mètre Radiometer.

On prélève 25 ml de cette solution qu'on verse dans la cellule d'électrolyse, et on ajoute 0.1 ml de la solution de gélatine.

Toutes les solutions mesurées sont débarrassées d'oxygène dissous par barbotage d'azote pur pendant 20 min. Un courant d'azote est maintenu au dessus de la solution pendant l'enregistrement des polarogrammes.

L'azote pur est obtenu par lavage de l'azote commercial dans une solution alcaline de pyrogallol, suivie d'une solution de Cr^{+2} dans l'acide sulfurique 1*M*, et d'eau distillée. La solution de Cr^{+2} est obtenue par réduction de Cr^{+3} à l'amalgame de Zn, dans un réducteur de Jones. Une quantité d'amalgame dans le flacon laveur empêche la réoxydation de Cr^{+2}.

Après 20 min de barbotage et après contrôle de la température (25°C), la pression du mercure est réglée pour obtenir une goutte par 3.8 sec dans la solution examinée. Le polarogramme de la solution est alors enregistré entre $E = 0$ V et $E = -1.50$ V.

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RÉSULTATS EXPÉRIMENTAUX

Domaine de stabilité des complexes de $Tl^+ + EDTA\ (H_4Y)$ *et* $Tl^+ + NTA\ (H_3X)$

Dans le Tableau I, nous avons résumé les valeurs $E_{\frac{1}{2}}$ et i_d (en μA) obtenues avec une une solution de Tl^+ de concentration finale $2 \cdot 10^{-4} N$, pour différents pH, en absence et en présence de EDTA et de NTA.

TABLEAU I

$E_{\frac{1}{2}}$ ET i_d EN FONCTION DU PH

pH	*conc.* K_2SO_4 *N*	*conc.* Tl^+ *N*	*conc.* *EDTA* *M*	$E_{\frac{1}{2}}$ *V*	i_d *μA*
3.86	$2 \cdot 10^{-1}$	$2 \cdot 10^{-4}$	.	—0.495	0.91
7.15	,,	,,	.	—0.486	0.93
9.09	,,	,,	.	—0.489	0.93
13.00	,,	,,	.	—0.491	0.925
3.94	,,	,,	10^{-1}	—0.496	0.84
6.10	,,	,,	10^{-1}	—0.510	0.625
7.08	,,	,,	10^{-1}	—0.584	0.48
7.67	,,	,,	10^{-1}	—0.626	0.49
8.74	,,	,,	10^{-1}	—0.688	0.49
9.62	,,	,,	10^{-1}	—0.728	0.49
10.25	,,	,,	10^{-1}	—0.746	0.48
10.43	,,	,,	10^{-1}	—0.748	0.48

pH	*conc.* *KCl* *N*	*conc.* Tl^+ *N*	*conc.* *NTA* *M*	$E_{\frac{1}{2}}$ *V*	i_d *μA*
4.05	1	$2 \cdot 10^{-4}$	.	—0.514	0.925
10.70	,,	,,	.	—0.518	0.91
4.90	,,	,,	$9.46 \cdot 10^{-2}$	—0.515	0.87
5.96	,,	,,	10^{-1}	—0.515	0.855
6.61	,,	,,	,,	—0.528	0.75
7.12	,,	,,	,,	—0.537	0.66
7.48	,,	,,	,,	—0.547	0.61
8.12	,,	,,	,,	—0.578	0.575
8.45	,,	,,	,,	—0.595	0.55
9.06	,,	,,	$9.46 \cdot 10^{-2}$	—0.616	0.52
9.90	,,	,,	10^{-1}	—0.641	0.54
10.40	,,	,,	$9.46 \cdot 10^{-2}$	—0.641	0.52

Les résultats sont représentés dans la Fig. 2 en fonction du pH. On peut constater qu'en présence d'un excès de EDTA le complexe se forme à partir de pH = 6 et que tout le Tl^+ est pratiquement complexé à partir de pH = 7. Avec un excès de NTA le complexe commence à se former également à partir de pH = 6, mais il faut aller jusqu'à pH = 9 pour obtenir un courant de diffusion constant indiquant que les ions Tl^+ ont été complètement complexés.

Les courbes de titrage obtenues en titrant avec une solution d'une base forte des solutions de EDTA et de NTA, avant et après addition d'un excès de Tl^+, sont représentées dans la Fig. 3. Elles confirment les résultats précédents. On en déduit également que le complexe de Tl^+ avec NTA est moins stable que celui avec EDTA.

Détermination des constantes de stabilité

Pour le calcul de la constante de stabilité nous utilisons la relation de LINGANE[7].

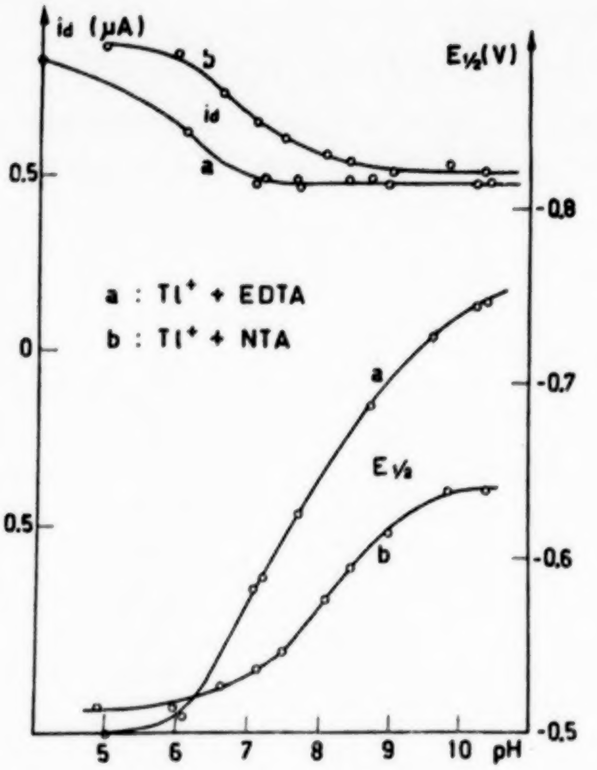

Fig. 2.

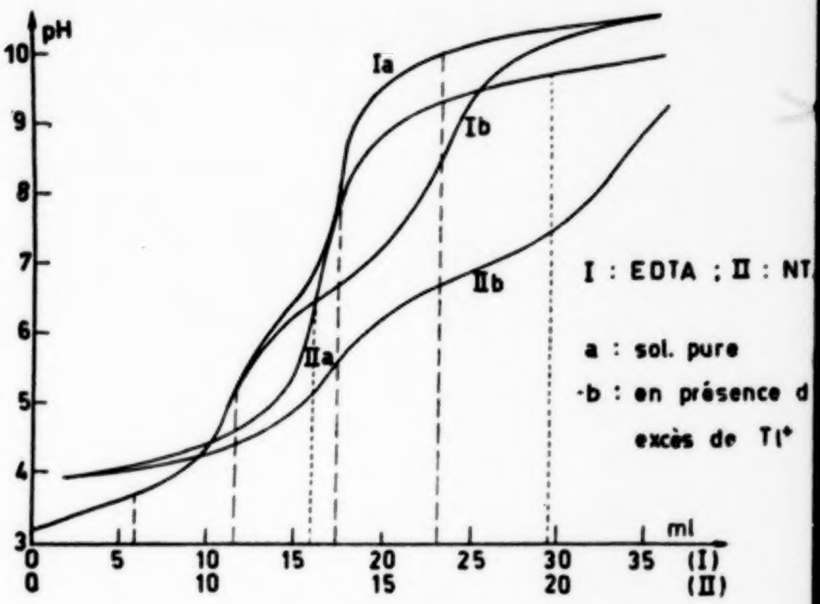

Fig. 3.

$$E_{\frac{1}{2}c} - E_{\frac{1}{2}s} = \frac{0.059}{n}\log\frac{K_c \cdot k_s}{k_c} - \frac{p}{n}\, 0.059 \log C_X$$

donnant le déplacement du potentiel demi-onde en fonction de la constante de stabilité K_c et de la concentration C_X de l'agent complexant.

$E_{\frac{1}{2}c}$ et $E_{\frac{1}{2}s}$	sont les potentiels demi-onde respectivement pour les ions complexés et pour les ions libres;
k_c et k_s	les constantes du courant de diffusion pour ces mêmes ions;
n	est le nombre d'électrons qui interviennent dans la réaction à l'électrode;
p	le nombre de molécules du complexant liées par ion Tl^+.

Cette relation est applicable à des systèmes réversibles, et à condition que la concentration de l'agent complexant puisse être considérée comme constante (grand excès).

Contrôle de la réversibilité

La réversibilité de la réaction à l'électrode a été contrôlée, pour les ions libres et pour les ions complexés, au moyen de la relation:

$$E = E_{\frac{1}{2}} - \frac{0.059}{n}\log\frac{i}{i_d - i}$$

qui implique une droite avec une pente de $\frac{0.059}{n}$ V pour le potentiel E en fonction de $\log\frac{i}{i_d - i}$.

Des mesures effectuées sur les polarogrammes enregistrés, ainsi que des mesures précises effectuées par opération manuelle, ont donné une droite pour les ions libres, ainsi que pour les ions complexés avec EDTA et avec NTA. La pente moyenne de la droite est de 0.0625 V entre pH 4 et 10 pour les ions libres, de 0.063 V entre pH 7 et 9 pour les ions complexés avec EDTA et entre pH 9 et 10 pour le complexe avec NTA.

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Ces valeurs correspondent sensiblement à la valeur théorique de 0.059 V pour $n = 1$. Le Tableau II donne la pente moyenne déterminée pour le complexe avec EDTA pour différents pH. Une des droites est représentée dans la Fig. 4.

TABLEAU II

RÉVERSIBILITÉ DE LA RÉACTION

pH	conc. Tl^+ N	conc. EDTA M	$\frac{dE}{d \log \frac{i}{i_d - i}}$
7.15	$2 \cdot 10^{-4}$	—	—0.0625 V
7.22	,,	10^{-1}	—0.0635 V
8.96	,,	$1.57 \cdot 10^{-2}$	—0.0625 V
8.96	,,	$5.63 \cdot 10^{-2}$	—0.0625 V
9.28	10^{-3}	$0.99 \cdot 10^{-1}$	—0.0630 V

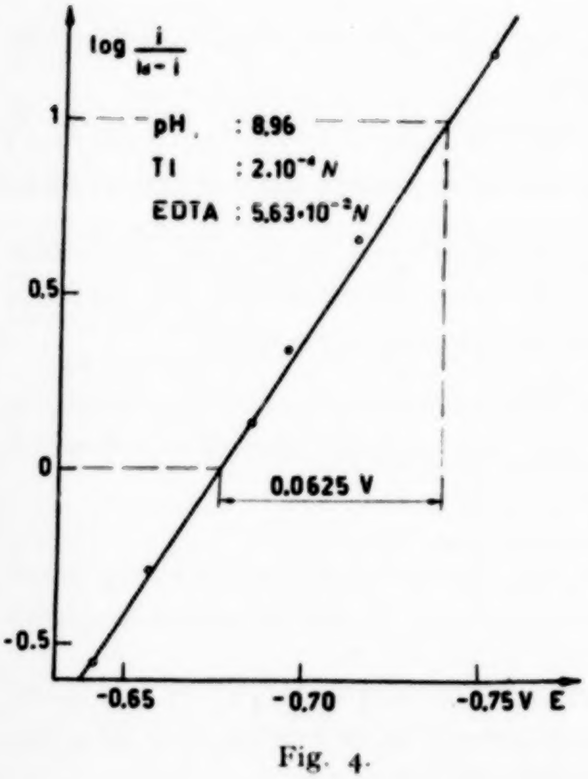

Fig. 4.

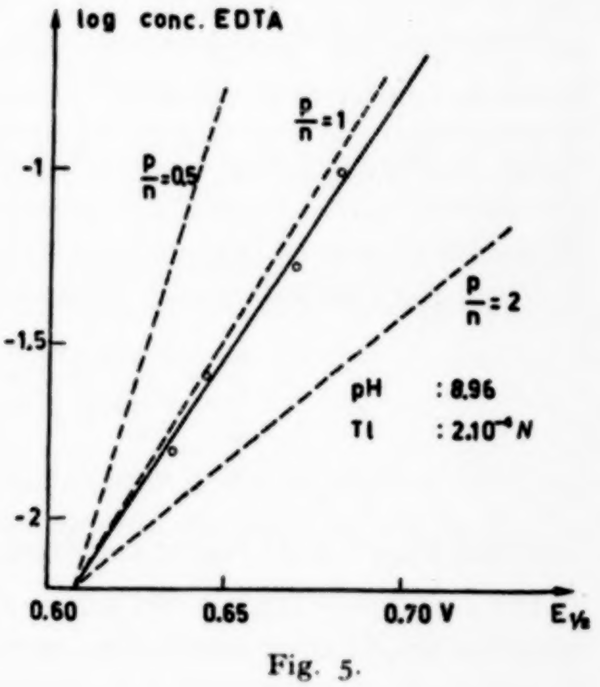

Fig. 5.

Le rapport $\frac{p}{n}$

LINGANE[7] a montré que le déplacement du potentiel $E_{\frac{1}{2}}$ en fonction de la concentration du complexant, toutes les autres conditions restant constantes, est donné par la relation simple:

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log C_X} = \frac{p}{n} \, 0.059$$

Pour la réaction $Tl^+ + e \rightleftarrows Tl$, $n = 1$.
Pour la détermination de p, plusieurs polarogrammes ont été enregistrés dans des conditions identiques, sauf pour la concentration de l'agent complexant.

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TABLEAU III

POTENTIEL $E_{\frac{1}{2}}$ EN FONCTION DE C_X

pH	*conc. Tl⁺* *N*	*conc.* K_2SO_4 *N*	*conc. EDTA* *M*	$E_{\frac{1}{2}}$ *V*
8.96	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1.57 \cdot 10^{-2}$	—0.635
8.96	,,	,,	$2.62 \cdot 10^{-2}$	—0.644
8.96	,,	,,	$5.63 \cdot 10^{-2}$	—0.670
8.96	,,	,,	$9.94 \cdot 10^{-2}$	—0.682

Le Tableau III donne les valeurs du potentiel $E_{\frac{1}{2}}$ en fonction de la concentration C_X de EDTA. Ces résultats sont représentés dans la Fig. 5 en même temps que les courbes théoriques pour les valeurs $\frac{p}{n} = 0.5$ — 1 et 2. La droite expérimentale obtenue avec le complexe $Tl^+ + EDTA$ indique un rapport $\frac{p}{n} = 1$. Nous avons obtenu un résultat analogue pour le complexe avec NTA.

Constantes du courant de diffusion

Les constantes du courant de diffusion peuvent être calculées moyennant la relation d'ILKOVIC à partir des courants limites de diffusion.

Pour le calcul de la constante de stabilité moyennant la relation de LINGANE, il suffit de connaître le rapport $\frac{k_s}{k_c}$. Comme tous les polarogrammes ont été pris avec le même capillaire et dans des conditions pratiquement identiques, ce rapport est donné directement par le rapport des courants limites de diffusion obtenus avec une solution d'ions libres et avec une solution d'ions complexés de concentration égale.

Moyennant les valeurs du Tableau I, nous calculons

$$\frac{k_s}{k_c} = \frac{0.925}{0.485} = 1.907 \text{ pour le complexe avec EDTA}$$

$$\frac{k_s}{k_c} = \frac{0.92}{0.53} = 1.735 \text{ pour le complexe avec NTA.}$$

Concentration C_X de l'agent complexant

Les courbes de titrage des acides éthylènediaminotétracétique (H_4Y) et nitrilotriacétique (H_3X) en présence d'un excès de Tl^+, montrent que la formation et la dissociation des complexes peut être représentée par les réactions suivantes:

1. $$Tl^+ + Y^{-4} \rightleftharpoons Tl\,Y^{-3}$$

$$K_c = \frac{[Tl^+]\,[Y^{-4}]}{[Tl\,Y^{-3}]}$$

2. $$Tl^+ + X^{-3} \rightleftharpoons Tl\,X^{-2}$$

$$K_c = \frac{[Tl^+]\,[X^{-3}]}{[Tl\,X^{-2}]}$$

Si les constantes d'acidité sont respectivement K_1, K_2, K_3 et K_4 pour le EDTA, et K_1', K_2' et K_3' pour le NTA, on calcule pour les concentrations C_X des ions complexants:

$$[Y^{-4}] = \frac{C_\circ - [Tl\,Y^{-3}]}{\Theta}$$

où
$$\Theta = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_4K_3} + \frac{[H^+]^3}{K_4K_3K_2} + \frac{[H^+]^4}{K_4K_3K_2K_1}$$

$$[X^{-3}] = \frac{C_0 - [\mathrm{Tl}\,X^{-2}]}{\Theta'}$$

où
$$\Theta' = 1 + \frac{[H^+]}{K_3'} + \frac{[H^+]^2}{K_3'K_2'} + \frac{[H^+]^3}{K_3'K_2'K_1'}$$

Les concentrations des complexes formés $[\mathrm{Tl}\,Y^{-3}]$ et $[\mathrm{Tl}\,X^{-2})$ étant toujours petites par rapport à C_0 en présence d'un excès suffisant des acides complexants, ces relations se simplifient:

$$[Y^{-4}] = \frac{C_0}{\Theta} \qquad \text{et } [X^{-3}] = \frac{C_0}{\Theta'}$$

Pour des solutions de pH > 7 la valeur de Θ est pratiquement déterminée par les 3 premiers termes, ainsi par K_3 et K_4; pour des solutions de pH > 8, la valeur de Θ' est déterminée par les deux premiers termes, c.à.d. par la constante K_3'.

SCHWARZENBACH, ACKERMANN ET RUCKSTUHL[8] ont trouvé la valeur $10^{-6.3}$ pour la constante K_3 de l'acide éthylènediaminotétracétique, dans un milieu à force ionique $\mu = 1$. On déduit la même valeur des travaux de CARINI ET MARTELL[9] qui ont étudié l'influence de la force ionique du milieu sur les constantes d'acidité. Ils trouvent des valeurs divergentes pour la constante K_4.

La constante K_3' de l'acide nitrilotriacétique a été déterminée par SCHWARZENBACH *et al.*[8] en milieu KCl 0.1*M*, où elle est $10^{-9.73}$. Elle est également fonction de la force ionique du milieu.

Les constantes K_4 et K_3' ont été déterminées expérimentalement par nous dans une solution de force ionique comparable à celle des solutions employées à l'enregistrement des polarogrammes. Nous avons trouvé respectivement:

$$K_4 = 10^{-9.95} \quad \text{et } K_3' = 10^{-9.35}.$$

Nous avons employé ces valeurs pour la calcul de Θ et Θ'. Celles-ci peuvent être lues directement sur la Fig. 6, qui donne ces valeurs en fonction du pH de la solution.

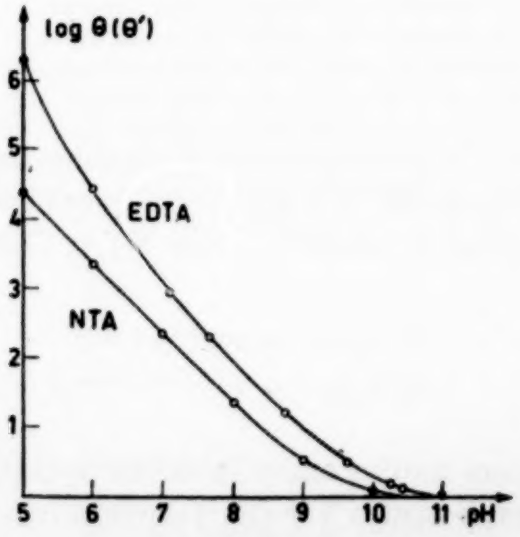

Fig. 6.

Constante de stabilité

On déduit de la relation de Lingane pour la constante de stabilité du complexe, posant:

$$C_X = [Y^{-4}] = \frac{C_\circ}{\Theta} \quad \text{et} \quad \frac{k_s}{k_c} = 1.907$$

$$\log K_{c(\text{EDTA})} = \frac{(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s}{0.059} - \log 1.907 + \log C_\circ - \log \Theta$$

posant

$$C_X = [X^{-3}] = \frac{C_\circ}{\Theta'} \quad \text{et} \quad \frac{k_s}{k_c} = 1.735$$

$$\log K_{c(\text{NTA})} = \frac{(E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s}{0.059} - \log 1.735 + \log C_\circ - \log \Theta'$$

Les valeurs des constantes $K_{c(\text{EDTA})}$ et $K_{c(\text{NTA})}$ ont été calculées pour différents pH moyennant ces relations et les données du Tableau I.

Les résultats sont résumés dans le Tableau IV.

TABLEAU IV

K_c (Tl⁺ — EDTA)

pH	*conc.* K_2SO_4 *N*	*conc.* Tl^+ *N*	*conc.* *EDTA* *M*	*log* Θ	$(E_{\frac{1}{2}})_c$ *V*	i_d *μA*	*μ*	K_c
7.08	$2\cdot10^{-1}$	$2\cdot10^{-4}$	10^{-1}	2.93	—0.584	0.48	0.90	$10^{-5.81}$
7.67	,,	,,	,,	2.30	—0.626	0.49	0.905	$10^{-5.86}$
8.74	,,	,,	,,	1.23	—0.688	0.49	0.95	$10^{-5.85}$
9.62	,,	,,	,,	0.50	—0.728	0.49	1.03	$10^{-5.81}$
10.25	,,	,,	,,	0.18	—0.746	0.48	1.15	$10^{-5.78}$
10.43	,,	,,	,,	0.12	—0.748	0.48	1.17	$10^{-5.75}$

K_c (Tl⁺ — NTA)

pH	*conc.* *KCl* *N*	*conc.* Tl^+ *N*	*conc.* *NTA* *M*	*log* Θ'	$(E_{\frac{1}{2}})_c$ *V*	i_d *μA*	*μ*	K_c
8.12	1	$2\cdot10^{-4}$	10^{-1}	1.25	—0.578	0.575	1.35	$10^{-3.58}$
8.45	,,	,,	,,	0.96	—0.595	0.55	1.37	$10^{-3.55}$
9.06	,,	,,	$9.46\cdot10^{-2}$	0.48	—0.616	0.52	1.42	$10^{-3.43}$
9.90	,,	,,	10^{-1}	0.11	—0.641	0.54	1.47	$10^{-3.47}$
10.40	,,	,,	$9.46\cdot10^{-2}$	0.05	—0.641	0.52	1.51	$10^{-3.41}$

Les constantes calculées sont pratiquement constantes dans le domaine de pH où les complexes se forment, c.à.d. de pH = 7 à pH = 10.5 pour le complexe avec EDTA, et de pH = 9 à pH = 10.5 pour le complexe avec NTA. Comme valeur moyenne nous trouvons:

$$K_{c(\text{EDTA})} = 10^{-5.81} \pm 0.05$$

$$K_{c(\text{NTA})} = 10^{-3.44} \pm 0.03$$

Pour des pH inférieurs aux limites citées la valeur de Θ (Θ') devient très grande, et la concentration des ions complexantes Y^{-4} (X^{-3}) devient très faible. Dans ces conditions la relation de LINGANE n'est plus strictement applicable.

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RÉSUMÉ

Le domaine de stabilité des complexes entre les ions Tl^+ et l'acide éthylènediaminotétracétique (EDTA) et entre les ions Tl^+ et l'acide nitrilotriacétique (NTA) a été déterminé. En présence d'un excès (100 ×) de complexant la formation des complexes commence à partir de pH = 6, elle est pratiquement complète à partir de pH = 7 pour le complexe avec EDTA, et à partir de pH = 9 pour le complexe avec NTA.

La réduction cathodique à l'électrode à gouttes de mercure est réversible aussi bien pour les ions Tl^+ complexés que pour les ions Tl^+ libres.

Les constantes de stabilité des complexes ont été déterminées par voie polarographique, moyennant le déplacement du potentiel demi-vague en fonction de la concentrration de l'agent complexant.

Les valeurs suivantes ont été trouvées:

$K_{c(\text{EDTA})} = 10^{-5.81 \pm 0.05}$ (25°C, $\mu = \pm 1.0$) de pH = 7 à pH = 10.5.
$K_{c(\text{NTA})} = 10^{-3.44 \pm 0.03}$ (25°C, $\mu = \pm 1.4$) de pH = 9 à pH = 10.5.

SUMMARY

The range of stability of the thallium complex with etylenediaminetetraacetic acid (EDTA) and with ammoniatriacetic acid (NTA) has been determined. In the presence of an excess (100 ×) of chelating agent, the formation of the complexes starts at pH = 6. Chelation of the metal with EDTA is practically complete at pH = 7, while completion of the chelation with NTA is reached merely at pH = 9.

The cathodic reduction of thallium(I) at the dropping mercury electrode is reversible as well for the chelated metal as for free Tl^+ ions.

The shift of the polarographic half wave potential of Tl^+ by addition of the chelating agents was used for the calculation of the stability constants of the chelates. The following values have been found:

$K_{c(\text{EDTA})} = 10^{-5.81 \pm 0.05}$ (25°C, $\mu = \pm 1.0$) between pH = 7 and pH = 10.5.
$K_{c(\text{NTA})} = 10^{-3.44 \pm 0.03}$ (25°C, $\mu = \pm 1.4$) between pH = 9 and pH = 10.5.

ZUSAMMENFASSUNG

Das Stabilitätsgebiet der Thalliumkomplexe der Äthylendiamintetraessigsäure (ÄDTE) und der Nitrilotriessigsäure (NTE) wurde bestimmt. In Gegenwart eines hundertfachen Überschusses an komplexierendem Reagens fängt die Komplexbildung bei pH = 6 an. Sie ist für das Komplex mit ÄDTE praktisch vollständig von pH = 7 an, aber für das Komplex mit NTE erst von pH = 9 an.

Die kathodische Reduktion an der Hg-Tröpfelelektrode verläuft umkehrbar, sowohl für die komplexierten Tl^+-ionen als für die freien Tl^+-ionen.

Die Stabilitätskonstanten der Komplexe wurden bestimmt durch Messung der durch Zusatz der Komplexbildner verursachten Verschiebung der polarographischen Halbstufenpotentiale.

Folgende Werte wurden gefunden:

$K_{c(\text{ÄDTE})} = 10^{-5.81 \pm 0.05}$ (25°C, $\mu = \pm 1.0$) zwischen pH = 7 und pH = 10.5.
$K_{c(\text{NTE})} = 10^{-3.44 \pm 0.03}$ (25°C, $\mu = \pm 1.4$) zwischen pH = 9 und pH = 10.5.

BIBLIOGRAPHIE

[1] G. Schwarzenbach *et al.*, *Helv. Chim. Acta*, 30 (1947) 1798; 32 (1949) 1543; 34 (1951) 1503.
[2] J. Koryta et I. Kossler, *Collection Czechoslov. Chem. Communs.*, 15 (1950) 241.
[3] J. Goffart, G. Michel et G. Duyckaerts, *Anal. Chim. Acta*, 9 (1953) 184.
[4] R. Pribil et Z. Zabransky, *Collection Czechoslov. Chem. Communs.*, 16-17 (1951-1953) 554.
[5] A. Heyndrickx et C. Collaer, *Compt. rend. 27e congr. intern. chim. ind. Bruxelles*, 2 (1954) 430.
[6] D. N. Hume et W. E. Harris, *Ind. Chem., Anal. Ed.*, 15 (1943) 465.
[7] J. J. Lingane, *Chem. Revs.*, 29 (1949) 1.
[8] G. Schwarzenbach, H. Ackermann et P. Ruckstuhl, *Helv. Chim. Acta*, 32 (1949) 1175.
[9] F. F. Carini et A. E. Martell, *J. Am. Chem. Soc.*, 74 (1952) 5745.

Reçu le 8 avril 1957

Short Communication

Dosage colorimétrique du fer par l'α,α'-dipyridyle

Ayant à déterminer la teneur en fer d'un alliage de platine nous avons voulu appliquer la méthode colorimétrique au dipyridyle[1,2,3].

On sait qu'en pareil cas il convient d'éliminer le platine, ce que nous avons réalisé en traitant la solution de l'échantillon par la poudre de zinc.

Après addition du réactif nous avons constaté que la teinte spécifique n'apparaissait pas, tandis qu'elle se développait normalement avec une solution dont le platine avait été précipité par l'hypophosphite de sodium.

Nous avons donc pensé qu'une quantité importante de zinc s'opposait au développement de la teinte que donne Fe^{2+} avec le dipyridyle.

Pour nous en assurer, nous avons appliqué la méthode à une solution M de chlorure de zinc renfermant des quantités connues de fer comprises entre 1 et 100 μg/ml, et observé qu'aucune teinte ne se développait.

Nous avons repris l'essai en faisant croître la quantité de zinc par rapport au fer.

A une solution titrant 100 γ Fe par ml nous avons ajouté des quantités connues de zinc comprises entre 1 et 100 γ par ml. Nous avons constaté que la teinte spécifique se développait normalement et que la méthode était fidèle tant que la valeur du rapport pondéral Zn/Fe restait inférieure à 25.

Au delà, la teinte va d'abord en s'affaiblissant, puis ne se développe plus.

Mme MARGUÉRITE GRAT-CABANAC

Faculté des Sciences de Toulouse (France)

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[1] M. Grat-Cabanac, *Anal. Chim. Acta*, 5 (1951) 116-118.
[2] M. Grat-Cabanac, *Anal. Chim. Acta*, 12 (1955) 50-53.
[3] M. Grat-Cabanac, *Anal. Chim. Acta*, 16 (1957) 150.

Reçu le 15 avril 1957.

REVUE DE LIVRE

Electrochemistry: Principles and Applications par **Edmund C. Potter**, Cleaver-Hume Press Ltd., Londres, 1956. Format 15/25, 430 pages, 122 figures, 4 planches hors texte. Prix 50 s.

Un livre d'électrochimie est directement utile à l'analyste dans la mesure où il apporte une aide pour résoudre les problèmes qui se posent dans le très vaste domaine où les réactions électrochimiques interviennent, dans la mesure aussi où il nous permet une conception plus claire des phénomènes que nous utilisons. Celui-ci est justement très clair et concis.

Après avoir traité des principes généraux, l'auteur utilise systématiquement les notions théoriques pour aborder les problèmes pratiques les plus importants. L'ouvrage est très moderne tant en ce qui concerne la partie théorique qui insiste sur l'aspect dynamique qu'en ce qui touche aux applications.

Les premiers chapitres, classiques en électrochimie, traitent des lois, de la conductance et des phénomènes de transport, des activités. On y trouvera la description des coulomètres. Un chapitre sur les équilibres ioniques est limité aux acides-bases et à l'hydrolyse selon la conception classique. Viennent ensuite des chapitres sur les potentials d'électrodes, les électrodes de référence, les processus irréversibles, la double couche. Les mesures électrochimiques et leurs applications analytiques sont traitées: conductimétrie, potentiométrie, mesure du pH, polarographie, ampérométrie, électrogravimétrie et coulométrie, en 50 pages environ. Ceci est très résumé, très concis et aussi très moderne. Rien ne figure sur les solvants autres que l'eau. L'électrophorèse et les membranes ne figurent pas.

Viennent ensuite les applications: de très beaux chapitres théoriques et pratiques sur la corrosion y compris les diagrammes potentiel-pH de Pourbaix et leurs aspects pratiques. Les principes des techniques électrochimiques sont traités: rendement en courant et énergie, dépôt des métaux et alliages, traitement électrolytique des minerais, raffinage des métaux, polissage électrolytique, sels fondus; enfin piles et accumulateurs. Toute la partie pratique est très claire et traitée constamment en liaison avec les notions théoriques.

La présentation du livre est très bonne.

Parmi les ouvrages d'électrochimie qu'un analyste garde en général à portée de la main, celui-ci est très certainement l'un des plus clairs et des plus modernes.

G. **Charlot** (Paris)

BUCHBESPRECHUNG

Massanalyse, Theorie und Praxis der klassischen und der elektrochemischen Titrierverfahren von G. **Jander und** K. F. **Jahr**. Verlag Walter de Gruyter & Co., Berlin, 1956. Sammlung Göschen, Band 221/221a. 7. ergänzte Aufl., 303 Seiten, 50 Abbildungen, geh. DM 4.80.

Die *Massanalyse* von **Jander und Jahr** liegt jetzt in der 7. Auflage vor. Nach einer Einführung in die praktischen Grundlagen werden die klassischen Methoden der Massanalyse: Oxydations- und Reduktionsanalysen, Neutralisationsanalysen und Fällungs- und Komplexbildungsanalysen besprochen. Dann folgen die elektrochemischen Methoden der Massanalyse, die Konduktometrie und Potentiometrie. Das Büchlein schliesst mit einem kurzen Überblick über die Geschichte der Massanalyse.

Gegenüber den älteren Auflagen sind einige wesentliche Erweiterungen und Verbesserungen vorgenommen worden. Einige veraltete Methoden wurden fortgelassen oder stark gekürzt, dafür wurden andere Kapitel — unter Berücksichtigung der modernen Auffassungen über die Reaktionsmechanismen — ausführlicher dargestellt, wie z.B. in der Manganometrie die Titration des Fe(II) in HCl-saurer Lösung, der Abschnitt über die Indikatortheorie, die Konstitution der Jodstärke oder — entsprechend ihrer zunehmenden Bedeutung — der Abschnitt über die Redoxindikatoren. Hinzu kommen eine ganze Reihe weiterer Ergänzungen und Modernisierungen. Neu aufgenommen wurden Beschreibungen des Jones-Reduktors, der Silberschichtbürette und der Glaselektrode als Indikatorelektrode in der Potentiometrie, sowie zwei kleine Kapitel über die Anwendung der Ionenaustauscher in der Neutralisationsanalyse und über die Chelatometrie. Auch die Nomenklatur wurde auf einen neueren Stand gebracht (wobei es allerdings konsequenterweise statt Cyanoferrat(4-) bzw. -(3-) auch Cyanoferrat(II) bzw. -(III) hätte heissen müssen). Als angenehm empfand es Ref. schliesslich, dass die bisher getrennten zwei Göschenbände jetzt in einem Doppelband vereinigt sind, wodurch die unglückliche Trennung mitten im Kapitel der Neutralisationsanalysen vermieden wurde.

Das kleine handliche Werk kann wegen seiner knappen und doch klaren und gut lesbaren Darstellung insbesondere Anfängern zur ersten Einführung empfohlen werden, wobei die zahlreichen Hinweise auf ausführlichere Werke (berücksichtigt bis 1955) ein vertieftes Studium ermöglichen. Aber auch ältere Studenten und Praktiker werden das Büchlein oft mit Vorteil zur Hand nehmen können.

F. **Umland** (Hannover)

BUCHBESPRECHUNG

Die Polarographie in der Medizin, Biochemie und Pharmazie von M. BŘEZINA UND P. ZUMAN, bearbeitete und ergänzte Übersetzung aus dem Tschechischen von H. BAŽANTOVÁ. Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig, 1956. 800 Seiten, mit 337 Abbildungen, DM 48.—.

Nachdem die Polarographie im Bereiche der anorganischen und organischen Analyse längst eingeführt wurde, begann sie nun in den letzten Jahren in das Gebiet der Biochemie, Pharmazie und Medizin vorzustossen. Schon sind sich sehr viele klinische Chemiker darüber einig, dass die polarographische Bestimmung von Metallen, wie z.B. Blei, im biologischen Material eines der sichersten und einfachsten Verfahren darstellt. Das Anwendungsgebiet blieb aber keineswegs auf die Metalle beschränkt, sondern erweiterte sich schnell auf organische Stoffe wie z.B. Alkaloide, Vitamine und Hormone. — Das vorliegende Werk stellt eine Zusammenfassung derjenigen polarographischen Veröffentlichungen dar, welche in der Biochemie, Pharmazie und Medizin angewandt werden können. Es ist aber nich nur eine bibliographische Zusammenfassung von 2000 Zitaten, sondern — wie der Begründer der Polarographie, Prof. HEYROVSKÝ, im Vorwort selber bestätigt — haben die Autoren die meisten Vorschriften und Reaktionen kritisch nachgeprüft und nach eigenen Erfahrungen bewertet. Dadurch entstand ein Werk, das mit seinen zahlreichen sehr klaren und meist einfachen Arbeitsvorschriften auch demjenigen von Nutzen sein kann, der bisher noch nicht polarographisch gearbeitet hat. Das Buch umfasst folgende Stoffgebiete:
Grundlagen der Polarographie (auf das Wichtigste beschränkt);
Bestimmung anorganischer Stoffe (Kationen und Anionen, Sauerstoff und Peroxyde);
Bestimmung organischer Stoffe (Chinone und andere Redoxsysteme, Halogenderivate, sauerstoffhaltige und stickstoffhaltige Stoffe, Alkaloide, Vitamine, Hormone und übrige Steroide, anodische Depolarisationen, versch. Verbindungen und indirekte Bestimmungen);
Eiweiss-Stoffe/Katalytische Wellen in Kobaltsalzlösungen;
Polarographische Studien enzymatischer Reaktionen;
Analytische Verwertung der Maxima.

Überdies enthält das sehr übersichtlich angeordnete Werk *Tabellen der wichtigsten Pufferlösungen* sowie *Tabellen der wichtigsten Halbstufenpotentiale* anorganischer und organischer Stoffe. Ausser dem Autoren- und Sachregister finden wir auch ein sorgfältig bearbeitetes Materialregister, wo die einzelnen Bestimmungen nach dem Untersuchungsmaterial angeordnet sind, das für den Mediziner, Biochemiker und Pharmazeuten in Frage kommt. — Wir sind davon überzeugt, dass das vorliegende Werk manchem forschenden oder praktisch arbeitenden Analytiker wesentlich zur Vereinfachung seiner Analysenverfahren beitragen wird.

W. F. RÜEDI (Genf)

REVUE DE LIVRE

Physical Methods in Chemical Analysis, Volume III, par WALTER G. BERL, Academic Press Inc., New York, 1956, 650 pages. Prix: $ 15.—. Le volume III de cette collection vient de sortir de presse. On y retrouve la bienfacture, la clarté et le soin qui caractérisent les ouvrages précédents. Les méthodes les plus récentes de l'analyse physico-chimique y sont décrites avec leurs applications pratiques principales. Il a été fait appel aux plus grands spécialistes du moment.

Le livre débute par la chromatographie gazeuse et les auteurs insistent sur l'importance de cette méthode qui permet de faire, en une même opération et rapidement, des séparations réputées difficiles et la détermination quantitative. Vient ensuite l'électrochromatographie, bases théoriques et appareillage. Les méthodes d'électro-analyse de traces font l'objet du 3ème chapitre; on y trouve entre autres les moyens techniques permettant d'augmenter la sensibilité d'appareils d'analyse physico-chimique. Citons encore parmi les plus importants chapitres les méthodes d'analyse chimique par haute fréquence, théorie et principes de l'échantillonnage, la spectrophotométrie de flamme. La spectroscopie des micro-ondes, les applications analytiques de la résonnace magnétique nucléaire, la distillation analytique et enfin un vaste exposé sur une toute nouvelle méthode d'investigation: la spectroscopie de neutron dans l'analyse chimique (neutron spectroscopy and neutron interreactions in chemical analysis.)

Cet excellent livre, indispensable aux chimistes analystes, donne de façon simple et claire les principes fondamentaux des diverses méthodes d'analyse physico-chimique. Il sera le bienvenu pour tous les spécialistes.

D. MONNIER (Genève)

THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

PART II. THE NITRONAPHTHYLAMINES AS NEW REAGENTS FOR MERCURIC MERCURY AND CERIC CERIUM

by

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INTRODUCTION

In Part I of this series, the use of the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid as a new spot test for stannous tin has been reported[1]. The application of this reagent has since been extended to the quantitative estimation of stannous tin[2].

Further investigation related to the reaction mechanism has indicated that two nitronaphthylamines can be used as specific spot tests and qualitative reagents for the detection of mercuric mercury and ceric cerium.

When used as a spot test for cations on filter paper, 4-nitro-1-naphthylamine yields an intense red coloration with mercuric nitrate, whereas 1-nitro-2-naphthylamine gives a vivid blue with ceric salts.

These two nitronaphthylamines are also suitable as qualitative reagents in inorganic analysis, mercuric nitrate giving a bright red precipitate in neutral or slightly acid media with 4-nitro-1-naphthylamine, whilst ceric salts yield an insoluble purple residue with 1-nitro-2-naphthylamine.

Thirteen of the possible fourteen nitronaphthylamines have been examined. Of 51 ions spot tested, ceric cerium alone gave a color reaction *immediately* with all isomers, the test being specific only in the case of the 1,2-compound. Ce^{+4} was the only ion to interfere in the mercuric mercury spot test.

EXPERIMENTAL

Synthesis of reagents

The nitronaphthylamines. The series of nitronaphthylamines is relatively easy to prepare, HODGSON AND HATHWAY[3] having summarised the available methods.

4-Nitro-1-naphthylamine 2-mercuriacetate. The procedure of HODGSON AND ELLIOTT[4] was used whereby a glacial acetic acid solution of 4-nitro-1-naphthylamine was heated with mercuric acetate to yield 4-nitro-1-naphthylamine 2-mercuriacetate. This was filtered, washed with water and then used immediately for the preparation of 2-chloro-4-nitro-1-naphthylamine.

2-Chloro-4-nitro-1-naphthylamine. An aqueous suspension of 4-nitro-1-naphthylamine 2-mercuriacetate (1 g) in 10% aqueous KCl was shaken with chlorine. The precipitated 2-chloro-4-nitro-1-naphthylamine was filtered, dried and recrystallised from alcohol. M.p. 249-50°C (ref. 4 : 249°C).

Spot test procedure

Approximately 0.02 ml of 0.1*M* aqueous solutions of the particular ions were spotted onto Whatman 3MM paper by means of a looped platinum wire. The paper was air-dried for ½-1 hour,

TABLE I

REAGENTS USED FOR SPOT TESTS

Reagent number	*Compound (1% solution in ethanol)*
1	2-nitro-1-naphthylamine
2	3-nitro-1-naphthylamine
3	4-nitro-1-naphthylamine
4	5-nitro-1-naphthylamine
5	6-nitro-1-naphthylamine
6	7-nitro-1-naphthylamine
7	8-nitro-1-naphthylamine
8	1-nitro-2-naphthylamine
9	4-nitro-2-naphthylamine
10	5-nitro-2-naphthylamine
11	6-nitro-2-naphthylamine
12	7-nitro-2-naphthylamine
13	8-nitro-2-naphthylamine

TABLE II

RESULTS OBTAINED ON SPRAYING SPOTS OF ION

Ion	*1*		*2*		*3*		*4*		*5*		*Reage* *6*	
	wet	*dry*	*wet*	*dry*	*wet*	*dry*	*wet*	*dry*	*wet*	*dry*	*wet*	*dry*
Cu^{+2}												
Ag^{+}		pale brown		brown		brown	pale green	deep green			yellow	yellow
Au^{+3}				purple		brown		blue			blue	purple
Hg^{+}		pink										
Hg^{+2}	pink	red			vivid red	deep red						
Ce^{+4}	blue	blue black	purple	purple	brown	brown	brown	brown	blue	purple	blue	purple
Cr^{+3}												
Cr^{+6}												
UO_2^{+2}												
Fe^{+2}							yellow	brown				
Fe^{+3}			pink	purple			green	green	brown	brown		
Ti^{+4}												

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then sprayed with a solution of the nitronaphthylamine reagent (1% in absolute alcohol with a trace of acetone where necessary to effect complete solubility). Any development of color was immediately noted, the paper then air-dried for 30 minutes and re-examined for any further color change. The reagents employed are listed in Table I; the results obtained are shown in Table II.

Sensitivity tests for mercuric mercury and ceric cerium were carried out using spots containing 0.02 ml of various concentrations of mercuric nitrate and cerium sulphate placed on sheets of filter paper. These spots were sprayed with the reagent which was specific for each ion, *e.g.* reagent nr 3 for mercuric nitrate and reagent nr 8 for cerium sulphate. The limit of sensitivity of the test was found to be 5 micrograms for mercuric mercury and 1 microgram of ceric cerium. In the case of ceric cerium, the blue spot was sensitive to 10 micrograms of material, but with 1 microgram there was a color change to red-brown. Tests were also performed with oxidising agents such as H_2O_2 and potassium permanganate but the only visible color change was with $KMnO_4$ when brown MnO_2 was precipitated at high concentration.

Further experiments were carried out using 2-chloro-4-nitro-1-naphthylamine as a reagent for mercuric mercury. The purpose of the test was to examine the effect of an *ortho-* halogen substituent in 4-nitro-1-naphthylamine upon the sensitivity of the reagent. In this case, it was observed that 2-chloro-4-nitro-1-naphthylamine did not give a red color change with mercuric nitrate.

Qualitative test procedure

The procedure adopted for qualitative test with cerium was to add an aqueous solution of a ceric salt ($0.1 M$) slowly to a 1% alcoholic solution of 1-nitro-2-naphthylamine whereupon a flocculent purple precipitate quickly formed. In the case of the mercury test, carefully controlled conditions were required before 4-nitro-1-naphthylamine yielded a bright red precipitate with mercuric nitrate. It was found necessary to add the reagent (1% in alcohol) to a neutral or slightly

TH VARIOUS REAGENTS BEFORE AND AFTER DRYING

mber 7		8		9		10		11		12		13	
et	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry	wet	dry
						pink	red	brown	dark brown				
						pale blue	green	pink	red				
ue	blue		brown		purple	yellow	yellow	pale blue	blue				
			pink										
ue	blue	blue	blue	purple	purple	black	black	blue	blue	blue	purple	blue	blue
	green brown												
							brown		brown				
				pale blue	deep purple				brown	pale brown	brown		brown
				orange	red								

Other ions tested were: Li$^+$, Na$^+$, K$^+$, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2} Al^{+3}, La^{+3},
$^{+3}$, Pr^{+3}, Nd^{+3}, Gd^{+3}, Sm^{+3} In^{+3}, Tl^{+3}, Zr^{+4}, Th^{+4}, Sn^{+2}, Sn^{+4}, Pb^{+2}, As^{+3}, As^{+5}, Sb^{+3},
$^{+3}$, Mo^{+6}, W^{+6}, Te^{+6}, Mn^{+2}, Co^{+2}, Ni^{+2}, Pt^{+2}, Ce^{+3}, VO^{+2}, VO$_3^-$, Tl$^+$.

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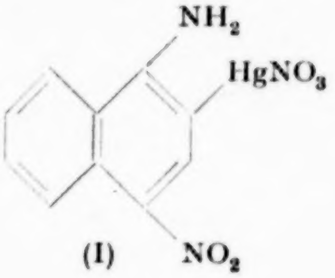
nitric acid solution of mercuric nitrate for ready precipitation. If the order of addition of reagents was reversed, precipitation of the mercuric compound was not immediately effected.

When mercuric chloride was used instead of mercuric nitrate, a yellow precipitate was readily formed. For spot test procedures, however, it was preferable to use mercuric nitrate since the red color change was more convenient for the identification of the cation.

DISCUSSION

The three nitronaphthylamines (*viz.* 2,1-,4,1- and 1,2 compounds) which give color reactions in the mercuric nitrate spot test are the weakest bases of the series. BRYSON[5] has discussed this phenomena in terms of acid-base equilibria and has shown that the pK_a values of these three isomers are approximately 2-3 units lower than the remainder of the series. The three compounds are also the most readily mercurated isomers in the series according to HODGSON[4,6,7], so that the effect of the nitro-group is to decrease the basic strength of the parent compound and to activate the ring containing the amino group towards mercuration, which occurs in the *ortho*- and *para*-positions.

Whether the spot test with mercuric nitrate is the result of such a mercuration reaction to yield 4-nitro-1-naphthylamine 2-mercuri-nitrate (I) or whether it is an organic coordination complex involving mercury^{II} has not been elucidated, however it is worthy of note that mercuric nitrate does not give a positive test with 4-nitro-1-naphthylamine when a halogen substituent blocks the *ortho*-position. Further work is in progress to clarify the mechanism of the reaction and to determine its practicability in quantitative analytical procedures.



(I)

The nature of the ceric cerium test has not yet been elucidated, although the precipitated material from the test has been isolated and found to contain cerium. More experimental data is required to discover whether this precipitate is an organic complex or whether it is an oxidation product of the nitronaphthylamine. The use of the reagent for quantitative cerium determinations is also being evaluated.

ACKNOWLEDGEMENT

The authors wish to thank Dr. A. BRYSON for some of the nitronaphthylamine preparations, also Dr. F. P. DWYER AND Mr. E. C. MARTIN for helpful discussion.

SUMMARY

The use of 4-nitro-1-naphthylamine as a spot test for mercuric mercury and 1-nitro-2-naphthylamine as a *specific* spot test for ceric cerium have been observed. In each case, the reactions appear to be suitable for general qualitative inorganic analysis. The ceric cerium test was specific whereas in the case of mercuric mercury, Ce^{+4} was the only ion of 51 tested which interfered.

RÉSUMÉ

On a étudié l'emploi de la 4-nitro-1-naphtylamine comme ,,spot test'' du mercure mercurique et la 1-nitro-2-naphtylamine comme ,,spot test'' spécifique pour le cérium cérique. Dans les deux cas, la réaction paraît applicable à l'analyse organique qualitative générale. Le test du cérium cérique est spécifique tandis que dans le cas du mercure mercurique, le Ce^{+4} est le seul ion qui gêne parmi les 51 essayés.

ZUSAMMENFASSUNG

Die Anwendung von 4-Nitro-1-naphtylamin als Tüpfelreagenz für zweiwertiges Quecksilber und von 1-Nitro-2-naphtylamin als spezifisches Tüpfelreagenz auf vierwertiges Cer wird beschrieben. Diese beiden Reaktionen scheinen in der allgemeinen qualitativen anorganischen Analyse anwendbar zu sein. Die Probe auf vierwertiges Cer war spezifisch, während im Falle des zweiwertigen Quecksilbers von 51 geprüften Ionen das Ce^{+4} das einzige war, welches störte.

REFERENCES

[1] J. R. A. ANDERSON AND J. L. GARNETT, *Anal. Chim. Acta*, 8 (1953) 393.
[2] J. R. A. ANDERSON AND S. LENZER LOWY, *ibid.*, 15 (1956) 246.
[3] H. H. HODGSON AND D. E. HATHWAY, *J. Soc. Dyers Col.*, 63 (1947) 231.
[4] H. H. HODGSON AND R. L. ELLIOTT, *J. Chem. Soc.*, (1934) 1705.
[5] A. BRYSON, *Trans. Faraday Soc.*, 45 (1949) 257.
[6] H. H. HODGSON AND R. L. ELLIOTT, *J. Chem. Soc.*, (1935) 1850.
[7] H. H. HODGSON AND R. L. ELLIOTT, *ibid.*, (1939) 345.

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A NEW ACID-BASE INDICATOR

by

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A spectrophotometric study of the iron(III)-1,2-dihydroxybenzene-3,5-disulfonic acid system has been made by YOE AND JONES[1]. They noted that the absorption characteristics of the system were pH dependent, but because they were primarily interested in other characteristics of the system, no detailed studies of the effect of pH were published. The present investigation was undertaken to further the study of color variations. These studies have shown that the changes in absorption characteristics are reversible and reproducible. The system seems well suited for use as an acid-base indicator and has the unique possibility that it may serve for double indicator titrations, as well as for use as a universal wide-range indicator.

EXPERIMENTAL

Apparatus and solutions

Spectrophotometric studies were made with a Beckman DK-1 Recording Spectrophotometer using 1.000 cm matched quartz cells.

Measurements of pH were made with a Beckman Model G pH Meter.

Buffer solutions were prepared according to Clark and Lubb's table[2].

The stock indicator solution was prepared in the following manner: 0.05 mole of Fe(III) (as ferric alum) and 0.15 mole of the sodium salt of 1,2-dihydroxybenzene-3,5-disulfonic acid were dissolved separately in small volumes of distilled water, mixed and filtered. The final volume was adjusted to 1 l with distilled water. Dissolution of the sodium salt of the disulfonic acid is more rapid in warm water.

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Experiments

Spectrophotometric studies were made on buffered solutions of the indicator mixture. 25 ml of the stock indicator solution were diluted to 250 ml with distilled water. 1 ml aliquots of this solution were adjusted to the approximate desired pH with sodium carbonate or hydrochloric acid and transferred to 50 ml volumetric flasks. The treated aliquots were then diluted to 50 ml with the appropriate buffer solution. For pH 13, final adjustement was made by the addition of sodium hydroxide solution.

Spectral absorption curves were obtained with the recording spectrophotometer and are given in Figs. 1 and 2. The numerical indexes of the curves correspond to the pH of the respective solutions, and two sets of curves are presented so that the complete pH-range involved is shown.

Table I summarizes the visual appearance of the hue and correlates the wavelength of maximum absorption and percentage transmission for the solutions at different pH-values.

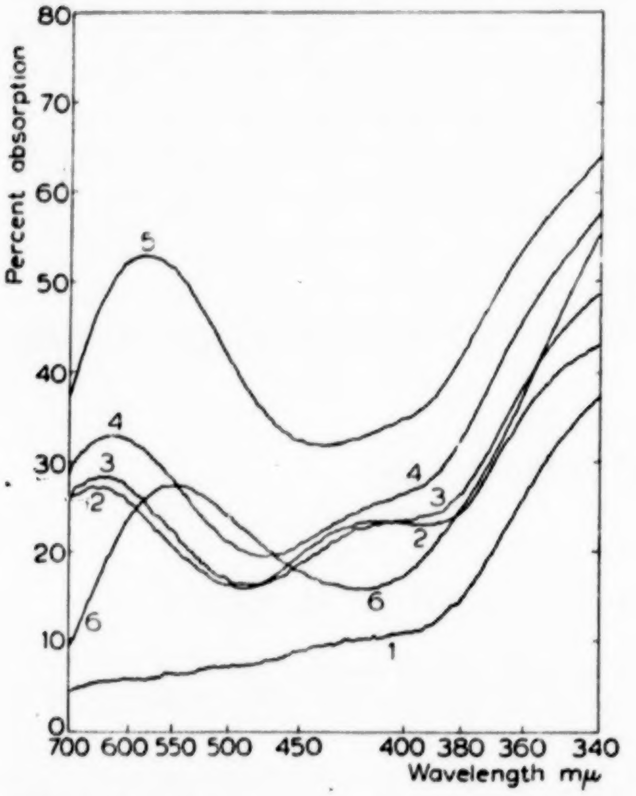

Fig. 1. Spectral absorption curves of iron(III)-1,2-dihydroxybenzene-3,5-disulfonic acid complex. Numerical index of the curves correspond to the pH of the system.

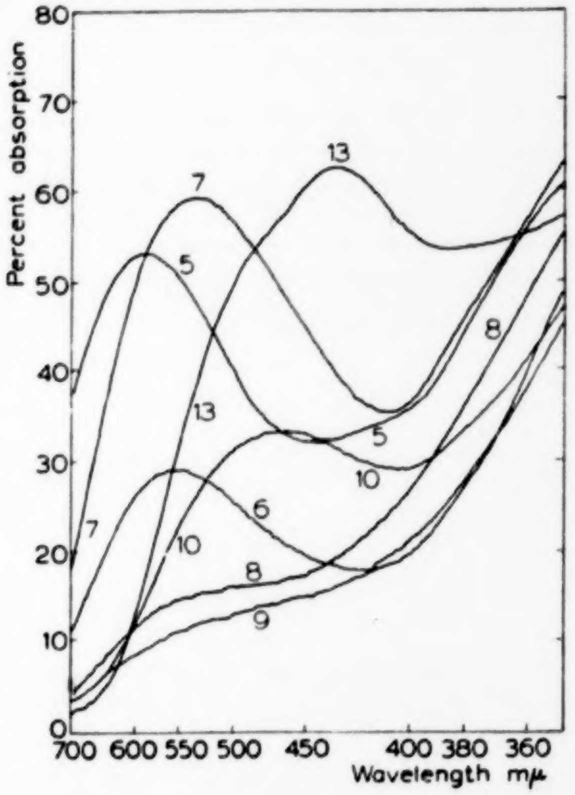

Fig. 2. Spectral absorption curves of iron(III)-1,2-dihydroxybenzene-3,5-disulfonic acid complex. Numerical index of the curves correspond to the pH of the system.

TABLE I

REGION OF MAXIMUM ABSORPTION

pH	*Wavelength of maximum absorption mμ*	*Transmission of absorption maximum %*	*Color of solution*
1	390	87.5	almost colorless with slight greenish tint
2	650	72.5	light green
3	650	71.0	green, deeper than pH 2
4	612	67.5	green, deeper than pH 3
5	565	55	blue
6	545	72.5	light violet
7	535	40	deep violet
8	600* and 430*	87.5 and 80	almost colorless with slight orange tint
9	600* and 430*	90 and 82.5	same as in pH 8
10	455	67.5	light orange
13	440	35.0	deep orange

* No peak, only an inflection.

DISCUSSION

Each of the buffered indicator solutions has a characteristic absorption maximum except at pH values of 1, 8, and 9. These latter solutions do not exhibit an absorption maximum in the visible spectrum, but absorption does increase toward the shorter wavelengths and inflections do occur in the spectra. The most pronounced shifts in the wavelength of maximum absorption occur over four distinct pH-ranges: 1-2, 4-6, 6-8, 8-10. Since the color changes are reversible and reproducible, the indicator may be used as a universal indicator.

Color changes over the pH-ranges 4-6 and 6-8 are distinct enough to make the indicator useful for strong acid-strong base and certain strong acid-weak base titrations. Acid-base volume ratios obtained using the new indicator compared favorably with the ratios obtained using modified methyl orange or phenolphthalein. Tables II and III compare data for titrations of sodium hydroxide and sodium carbonate solutions with hydrochloric acid using different indicators. Titrations using the new indicator were stopped as the color changed from violet to green, pH 6 to 4. The experimental acid-base ratios correspond closely to that calculated for each indicator.

TABLE II

VOLUME OF 0.1N HCl REQUIRED TO TITRATE 25.00 ml ALIQUOTS OF A 0.05N NaOH SOLUTION WITH DIFFERENT INDICATORS

Solutions	*Modified methyl orange*	*Phenolphthalein*	*New indicator*
A	13.85	13.60	13.65
	13.83	13.60	13.70
	13.83	13.59	13.70
	13.83	13.54	13.70
		13.60	13.70
			13.73
B	12.00	11.88	11.82
	11.98	11.86	11.82
	12.00	11.82	11.86
	12.00	11.86	11.80
C	12.00		11.80
	12.00		11.82
	12.01		11.80
			11.81

TABLE III

VOLUME OF 0.1N HCl REQUIRED TO TITRATE 25.00 ml ALIQUOTS OF A 0.1N Na_2CO_3 SOLUTION WITH DIFFERENT INDICATORS

Solutions	*Modified methyl orange*	*New indicator*
A	23.94	23.70
	23.95	23.70
	23.97	23.69
	23.93	23.69
	23.93	23.71
		23.70
B	24.72	24.45
	24.70	24.48
	24.72	24.46
		24.48

The discrepancy in the titer-values using different indicators is quite obvious, due to the location of the region of pH change on the pH curve. The extent of possible error using different indicators is shown in Fig. 3. The experimental values obtained with the new indicator compare favorable with the theoretical calculations.

Encouraged by the preliminary results obtained, the indicator was introduced to elementary quantitative analysis classes to be used for the comparison of hydrochloric acid and sodium hydroxide solutions and for the determination of soda ash. No consistent difference was detected in the student results obtained by those using the new indicator and those using modified methyl orange. The students preferred the color change of the new indicator at the end-point to that observed for modified methyl orange.

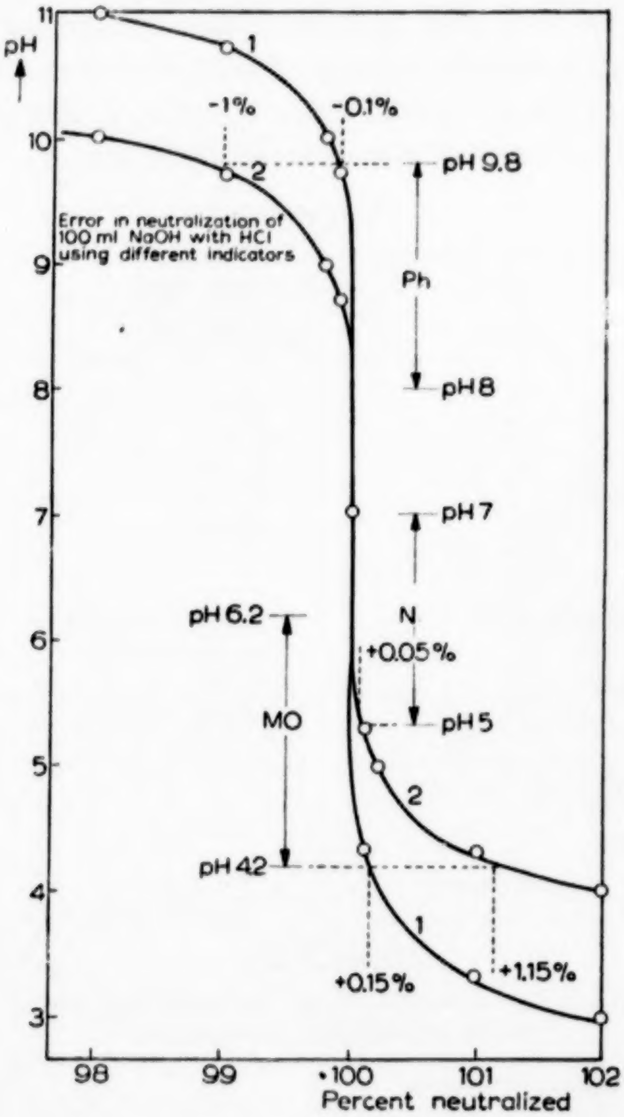

Fig. 3. Error in neutralization of 100 ml NaOH with HCl using different indicators: Ph = Phenolphthalein; MO = Modified methyl orange; N = New indicator. Curve 1: 0.1 N solutions; Curve 2: 0.01 N solutions.

Solutions of the indicator below pH 6 are not stable at the boiling point. The decomposition product is yellow-brown but not intense enough to interfere with subsequent titration. Upon cooling, additional indicator may be added and the titration continued. Solutions with a pH greater than 7 may be boiled without adversely affecting the indicator.

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The iron(III)-1,2-dihydroxybenzene-3,5-disulfonic acid system has promise as an indicator for neutralization involving strong electrolytes. Its color characteristics also suggest a possible use as a universal indicator.

SUMMARY

The Fe(III)-1,2-dihydroxybenzene-3,5-disulfonic acid complex absorption characteristics are pH dependent. An intensive study has shown that these characteristics are reversible and reproducible.

This system is, therefore, well-suited for use as a pH indicator. It serves for double indicator titrations (acid → base; base → acid) and as a universal wide-range indicator.

RÉSUMÉ

Le système Fe(III) - acide-1,2-dihydroxybenzène-3,5-disulfonique a des caractéristiques d'absorption, dépendant du pH. Une étude approfondie a montré que les changements de ces caractéristiques sont réversibles et reproductibles.

Le sytème mentionné peut donc être utilisé comme indicateur de pH. Il sert de double indicateur dans les titrations (acide → base; base → acide) et d'indicateur sur une large étendue de l'échelle des pH.

ZUSAMMENFASSUNG

Die Absorption des Systemes Fe(III)-1,2-Dioxybenzol-3,5-disulfosäure hängt vom pH ab. Eine eingehende Untersuchung hat gezeigt, dass die Änderungen der Absorptionswerte reversibel und reproduzierbar sind.

Das genannte System kann daher als pH-Indikator verwendet werden. Es dient als doppelter Indikator bei den Titrationen (Säure → Base; Base → Säure) und als Indikator für einen grossen pH-Bereich.

REFERENCES

[1] J. H. YOE AND A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 111.

[2] *Langes Handbook of Chemistry*, 7th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1127.

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THE GRAVIMETRIC DETERMINATION OF TUNGSTEN IN TUNGSTATE SOLUTIONS

by

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INTRODUCTION

The methods used for the gravimetric determination of tungsten can be divided into three groups: (a) precipitation as Hg-, Pb-, Ba- or Ca-tungstates; (b) precipitation in acid medium as insoluble WO_3; (c) precipitation in the presence of organic reagents. Especially in the last group, a variety of methods has been described, but these have not always proved satisfactory in later investigations.

The hydrazine hydrochloride method[1] was later replaced by *o*-tolidine[2] or benzidine[3], and later again by α-naphthylamine[4]. As precipitation with gallic acid or digallic acid[5,6,7] needs a long digestion time and seems to be incomplete, the use of mixtures such as tannin and phenazone[8,9], tannin and cinchonine[10,11] or tannin, cinchonine and phenazone[12,13] is preferred.

Different reagents have been reported to give good results, but also give similar precipitation reactions with Mo or V; among these are several aromatic amines, *e.g.* cumidine, tetramethyl-4-4′-diaminobenzophenone, tetra-methyl-*p*-diaminodiphenylmethane[14], nitron[15], phenylhydrazine[16], aluminon[17], α-benzoinoxime[18,19] 8-hydroxyquinoline[20], vanillidene-benzidine and *p*-dimethylamino-benzilidene-benzidine[21].

The quinine-acetate method[22], introduced in 1882, was later replaced by cinchonine[23,24]. With this reagent, good results were obtained by several investigators[25,26], although other workers did not find it satisfactory[27,11]. Later again, this reagent was replaced by β-naphthoquinoline[28] and rhodamine B[29], which was reported to be better than cinchonine[27].

As already mentioned, several of the original procedures have been modified by later workers and some reagents have been repeatedly replaced by so-called better ones. This indicates that some of these methods are not satisfactory and cannot be used successfully for the quantitative gravimetric determination of tungsten. As a matter of fact, a theoretical selection between these procedures is difficult, so that a comparative survey of the different methods is needed. However, a first selection can be made: since it is our intention to determine tungsten in the presence of molybdenum or vanadium, only those methods which do not give similar precipitation reactions with Mo or V will be studied.

REFERENCE METHOD

Choice of the method

This choice could not be determined by the specific character of the reagent, but only by the quantitative formation of the precipitate. Therefore, since the formation of insoluble WO_3 needs repeated treatment with acids for more or less total precipitation, this method cannot be used. Obviously, the organic reagents that are to be tested in this study must also be excluded as reference method. The precipitation as Pb-, Ba- or Cd-tungstate[30] is difficult to use, due to the unknown composition of the precipitate and the lack of an ideal ignition temperature[31]. On the other hand, the use of $Hg_2(NO_3)_2$, introduced by BERZELIUS[32], is reported to give excellent results: it produces a quantitative formation of Hg_2WO_4 by single precipitation and can be ignited to WO_3 as the stable ignition form. This last method was chosen as reference method.

Experimental

The precipitation can be carried out in slightly acid or ammoniacal medium. In order to make a comparison, the two methods were examined similarly as follows:

(a) Acid medium: 25 ml of the alkali-tungstate solution are neutralized (methyl orange) with a few drops of 3*N* HNO_3, and heated to boiling point, with constant stirring. 10 ml of a $Hg_2(NO_3)_2$ solution [saturated solution of $Hg_2(NO_3)_2$ in 0.075 *N* HNO_3] are added drop by drop.

After the precipitate has settled, filtration is made on a Schleicher and Schull 589[3] filter, and the precipitate is washed with a hot, dilute (1:5) solution of the reagent. The precipitate is ignited at 850°C and weighed as WO_3.

(b) Alkaline medium: After formation of the precipitate in the same way, a few drops of 6*N* NH_4OH are added, color changing from yellow to gray. The solution is heated for 5 minutes and treated again with NH_4OH if the precipitate becomes yellow. After digestion for 5 minutes, the solution is filtered, the precipitate washed with a hot, dilute (1:20) reagent-solution and ignited at 850°C.

The results are given in Table I.

TABLE I

	Acid medium			*Ammoniacal medium*		
	WO_3 *mg*	*Deviation from average value* *mg*	*Deviation from average value* %	WO_3 *mg*	*Deviation from average value* *mg*	*Deviation from average value* %
	316.1	−0.5	−0.16	316.8	−0.1	−0.03
	316.4	−0.1	−0.06	316.8	−0.1	−0.03
	316.6	0.0	0.0	316.9	0.0	0.0
	316.7	+0.1	+0.03	316.9	0.0	0.0
	317.0	+0.4	+0.13	317.0	+0.1	+0.03
average	316.6	0.2	0.08	316.9	0.1	0.02

Conclusion

The results are satisfactory with both methods. Due to its greater precision, determination in slightly ammoniacal solution with $Hg_2(NO_3)_2$ was adopted as reference method.

PRECIPITATION AS WO_3

Principle of the method

In the classical method the WO_3 is made insoluble by HCl + HNO_3, followed by repeated evaporation to dryness in the presence of the acids. However, in order to avoid co-precipitation which always occurs with this method, some authors suggest digestion of the precipitate in the presence of the acid. The quantitative character of this procedure is examined, using HCl, HNO_3, H_2SO_4 and $HClO_4$.

Experimental

Precipitation was carried out in three different ways, each time using 25 ml of the tungstate solution (316.9 mg WO_3). In all of these methods, filter-pulp was used and the precipitate was ignited at 850°C.

Method 1. 10 ml of the concentrated acid are added drop by drop, while stirring, to the tungstate solution, which is then heated to boiling point, treated with a few drops of conc. HNO_3, and heated again for 5 minutes. After digestion for one hour on a steam bath, the hot solution is filtered and the precipitate washed with a hot acid solution.

Method 2. The precipitate is formed at room temperature by adding 10 ml of the acid drop by drop, followed by a few drops of conc. HNO_3. After digestion at room temperature for 12 hours, the solution is filtered and the precipitate washed with a cold acid solution.

Method 3. The tungstate solution is heated to boiling point, and 10 ml of conc. acid, followed by a few drops of conc. HNO_3, are added. After digestion at room temperature for 12 hours, the solution is filtered off and the precipitate is washed with a cold acid solution.

As reagents, the following acids were used:
12*N* HCl wash liquid: 4*N* HCl
14*N* HNO_3 wash liquid: 4*N* HNO_3
12*N* H_2SO_4 wash liquid: 4*N* H_2SO_4
70% $HClO_4$ wash liquid: 4*N* HCl
The results are given in Table II.

TABLE II

Method	*WO_3*	*Deviation from average value*		*Deviation from true value*	
	mg	*mg*	%	*mg*	%
HCl, method 1	304.1	—2.6	—0.85	—12.8	—4.0
	305.3	—1.4	—0.46	—11.6	—3.7
	307.5	+0.8	+0.26	—9.4	—3.0
	307.8	+1.1	+0.36	—9.1	—2.9
	308.6	+1.9	+0.62	—8.3	—2.6
average	306.7	1.6	0.51	—10.2	—3.2
HCl, method 2	304.0	—2.2	—0.72	—12.9	—4.1
	304.5	—1.7	—0.55	—12.4	—3.9
	305.2	—1.0	—0.33	—11.7	—3.7
	306.1	—0.1	—0.03	—10.8	—3.4
	311.2	+5.0	+1.63	—5.7	—1.8
average	306.2	2.0	0.65	—10.7	—3.4
HCl, method 3	303.1	—2.1	—0.69	—13.8	—4.4
	304.1	—1.1	—0.36	—12.8	—4.1
	304.3	—0.9	—0.29	—12.6	—4.0
	305.5	+0.3	+0.10	—11.4	—3.6
	309.2	+4.0	+1.31	—7.7	—2.4
average	305.2	1.7	0.56	—11.7	—3.7
HNO_3, method 1	305.9	—1.9	—0.62	—11.0	—3.5
	307.0	—0.8	—0.26	—9.9	—3.1
	308.7	+0.9	+0.29	—8.2	—2.6
	308.8	+1.0	+0.33	—8.1	—2.5
	308.8	+1.0	+0.33	—8.1	—2.5
average	307.8	1.1	0.37	—9.1	—2.8

TABLE II (continued)

Method	*WO_3*	*Deviation from average value*		*Deviation from true value*	
	mg	*mg*	%	*mg*	%
HNO_3, method 2	305.1	−2.4	−0.78	−11.8	−3.7
	307.1	−0.4	−0.31	−9.8	−3.1
	307.9	+0.4	+0.13	−9.0	−2.8
	308.6	+1.1	+0.36	−8.3	−2.6
	308.9	+1.4	+0.46	−8.0	−2.5
average	307.5	1.1	0.37	−9.4	−2.9
HNO_3, method 3	304.8	−2.0	−0.65	−12.1	−3.8
	306.0	−0.8	−0.26	−10.9	−3.4
	307.6	+0.8	+0.26	−9.3	−3.0
	307.7	+0.9	+0.29	−9.2	−2.9
	307.9	+1.1	+0.36	−9.0	−2.8
average	306.8	1.1	0.36	−10.1	−3.2
H_2SO_4, method 1	270.1	−4.3	−1.57	−46.8	−14.8
	272.2	−2.2	−0.80	−44.7	−14.1
	274.5	+0.1	+0.04	−42.4	−13.4
	277.2	+2.8	+1.02	−39.7	−12.5
	277.9	+3.5	+1.28	−39.0	−12.3
average	274.4	2.6	0.94	−42.5	−13.4
H_2SO_4, method 2	274.9	−3.7	−1.33	−42.0	−13.2
	276.2	−2.4	−0.86	−40.7	−12.8
	278.7	+0.1	+0.04	−38.2	−12.0
	280.1	+1.5	+0.54	−36.8	−11.6
	282.9	+4.3	+1.54	−34.0	−10.7
average	278.6	2.4	0.86	−38.3	−12.1
H_2SO_4, method 3	274.9	−2.8	−1.01	−42.0	−13.2
	275.9	−1.8	−0.65	−41.0	−12.9
	278.5	+0.8	+0.29	−38.4	−12.1
	279.2	+1.5	+0.54	−37.7	−11.9
	280.1	+2.4	+0.87	−36.8	−11.6
average	277.7	1.9	0.67	−39.2	−12.3
$HClO_4$, method 1	312.5	−0.8	−0.25	−4.4	−1.4
	313.0	−0.2	−0.10	−3.9	−1.2
	313.5	+0.2	+0.06	−3.4	−1.1
	313.6	+0.3	+0.10	−3.3	−1.0
	313.7	+0.4	+0.13	−3.2	−1.0
average	313.3	0.4	0.13	−3.6	−1.1
$HClO_4$, method 2	312.0	−0.8	−0.26	−4.9	−1.6
	312.4	−0.4	−0.13	−4.5	−1.4
	312.8	0.0	0.0	−4.1	−1.3
	313.2	+0.4	+0.13	−3.7	−1.2
	313.4	+0.6	+0.19	−3.5	−1.1
average	312.8	0.4	0.14	−4.1	−1.3
$HClO_4$, method 3	311.6	−0.9	−0.29	−5.3	−1.7
	312.0	−0.5	−0.16	−4.9	−1.6
	312.9	+0.4	+0.13	−4.0	−1.3
	313.0	+0.5	+0.16	−3.9	−1.2
	313.1	+0.6	+0.19	−3.8	−1.2
average	312.5	0.6	0.19	−4.4	−1.4

Discussion

The results in Table II clearly indicate a considerable deviation from the value obtained with the $Hg_2(NO_3)_2$ reference method, especially by using H_2SO_4 (12-18%). Neither HCl nor HNO_3 is a satisfactory reagent (3—3.5% error). The best results are obtained using $HClO_4$; although the precision is rather good (0.13%), the values still indicate a loss of 1% WO_3.

This means that the precipitation of WO_3 by acids, followed by a digestion in the presence of the acid, does not give quantitative results, and cannot be used for the quantitative determination of tungsten from alkali-tungstate solutions.

PRECIPITATION WITH ORGANIC REAGENTS IN ACID MEDIUM

Experimental

In the following procedures, 25 ml of a tungstate-solution (316.9 mg WO_3 in the reference method) are used. The reagent solutions are added drop by drop, under stirring, and filter pulp is always used. The filtration is made on a Schleicher and Schull 589^3 filter, and the precipitates are ignited at 850°C.

(a) Phenazone. 10 ml 12*N* HCl, 5 ml phenazone solution (5% in water) and a few drops of conc. HNO_3 are added to the cold solution. After boiling for 5 minutes and digesting at room temperature for 3 hours, the cold solution is filtered and the precipitate washed with a cold dilute solution of the reagent (0.1% phenazone in 0.2*N* HCl).

(b) Cinchonine. The tungstate solution is acidified with 10 ml 12*N* HCl, heated to boiling point, and treated with a few drops of conc. HNO_3.

After addition of 3 ml cinchonine reagent (12.5% in 6*N* HCl), the solution is boiled for 5 minutes, and heated on a steam bath until the supernatant liquid is clear. The hot solution is filtered and washed with a hot 1:30 solution of the reagent.

(c) Tannin. After addition of 10 ml 12*N* HCl, 10 ml of a freshly prepared 10% tannin solution in water, and a few drops of conc. HNO_3, the solution is boiled for 5 minutes. After digestion on a steam bath for one hour, the voluminous precipitate has to be cooled thoroughly before filtering off and washing it with a cold tannin solution (0.5% in 1*N* NH_4Cl).

(d) Tannin + cinchonine. As in tannin method; a mixture of 5 ml 10% tannin in water and 5 ml 12.5% cinchonine in 6*N* HCl is used as reagent. The wash liquid is made by dissolving 0.5 g tannin and 0.4 g cinchonine in 100 ml 0.2*N* HCl.

(e) Tannin + phenazone. This procedure is similar to the tannin method. The reagent is a mixture of 5 ml 10% tannin in water and 5 ml 5% phenazone in water. The wash liquid is a solution of 0.5% tannin and 0.1% phenazone in 0.2*N* HCl.

(f) Benzidine. The solution, acidified with 10 ml 12*N* HCl, is heated, and 3 ml benzidine solution (2% in 0.25*N* HCl) are added. After boiling for 5 minutes, the solution is cooled thoroughly before filtration. The wash liquid is a cold, dilute solution of the reagent (0.1% in 0.1*N* HCl).

(g) o-Tolidine. This method, similar to the benzidine method, uses 15 ml of an *o*-tolidine solution (2% *o*-tolidine in 0.3*N* HCl) as reagent and a solution of 0.1% *o*-tolidine in 0.1*N* HCl as wash liquid.

(h) Rhodamine B. The acidified solution is treated at room temperature with 10 ml 12*N* HCl, 5 ml 1% rhodamine B solution in water, a few drops of conc. HNO_3, and is boiled for 5 minutes. After digestion on a steam bath, the hot solution is filtered and the precipitate washed with a hot 0.001% rhodamine B solution.

(i) β-Naphthoquinoline. The solution is acidified with 10 ml 12*N* HCl, and a few drops of conc. HNO_3. The solution is heated, and 3 ml of β-naphthoquinoline solution (2% in 0.6*N* H_2SO_4) are added. After digestion on the steam bath for half an hour, the hot solution is filtered and the precipitate washed with a hot solution of β-naphthoquinoline (0.02% in 0.2*N* H_2SO_4).

The results are given in Table III.

TABLE III

Method	*WO_3*	*Deviation from average value*		*Deviation from true value*	
	mg	*mg*	%	*mg*	%
Phenazone	314.0	−0.4	−0.13	−2.9	−0.91
	314.2	−0.2	−0.06	−2.7	−0.85
	314.3	−0.1	−0.03	−2.6	−0.82
	314.7	+0.3	+0.10	−2.2	−0.69
	315.0	+0.6	+0.19	−1.9	−0.60
average	314.4	0.3	0.10	−2.5	−0.77
Cinchonine	316.1	−0.5	−0.16	−0.8	−0.25
	316.5	−0.1	−0.03	−0.4	−0.13
	316.7	+0.1	+0.03	−0.2	−0.06
	316.8	+0.2	+0.06	−0.1	−0.03
	316.9	+0.3	+0.10	0.0	0.0
average	316.6	0.2	0.08	−0.3	−0.09
Tannin	312.6	−0.5	−0.16	−4.3	−1.36
	312.9	−0.2	−0.06	−4.0	−1.26
	313.0	−0.1	−0.03	−3.9	−1.23
	313.2	+0.1	+0.03	−3.7	−1.17
	313.6	+0.5	+0.16	−3.3	−1.04
average	313.1	0.3	0.09	−3.8	−1.21
Tannin + cinchonine	316.1	−0.4	−0.13	−0.8	−0.25
	316.3	−0.2	−0.06	−0.6	−0.19
	316.6	+0.1	+0.03	−0.3	−0.09
	316.7	+0.2	+0.06	−0.2	−0.06
	316.8	+0.3	+0.10	−0.1	−0.03
average	316.5	0.2	0.08	−0.4	−0.12
Tannin + phenazone	314.1	−0.6	−0.19	−2.8	−0.88
	314.3	−0.4	−0.13	−2.6	−0.82
	314.6	−0.1	−0.03	−2.3	−0.72
	314.9	+0.2	+0.06	−2.0	−0.63
	315.4	+0.7	+0.22	−1.5	−0.47
average	314.7	0.4	0.13	−2.2	−0.70
Benzidine	313.8	−0.4	−0.13	−3.1	−0.98
	314.1	−0.1	−0.03	−2.8	−0.88
	314.3	+0.1	+0.03	−2.6	−0.82
	314.3	+0.1	+0.03	−2.6	−0.82
	314.6	+0.4	+0.13	−2.3	−0.72
average	314.2	0.2	0.07	−2.7	−0.86
o-Tolidine	313.5	−0.9	−0.23	−3.4	−1.07
	314.2	−0.2	−0.06	−2.7	−0.85
	314.5	+0.1	+0.03	−2.4	−0.76
	314.9	+0.5	+0.16	−2.0	−0.63
	315.0	+0.6	+0.19	−1.9	−0.60
average	314.4	0.5	0.13	−2.5	−0.78
Rhodamine B	314.6	−0.3	−0.10	−2.3	−0.72
	314.7	−0.2	−0.06	−2.2	−0.69
	314.9	0.0	0.0	−2.0	−0.63
	315.1	+0.2	+0.06	−1.8	−0.57
	315.3	+0.4	+0.13	−1.6	−0.50
average	314.9	0.2	0.07	−2.0	−0.62

TABLE III (continued)

Method	WO_3	*Deviation from average value*		*Deviation from true value*	
	mg	*mg*	%	*mg*	%
β-Naphthoquinoline	316.6	−0.1	−0.03	−0.3	−0.09
	316.6	−0.1	−0.03	−0.3	−0.09
	316.7	0.0	0.0	−0.2	−0.06
	316.8	+0.1	+0.03	−0.1	−0.03
	317.0	+0.3	+0.10	+0.1	+0.03
average	316.7	0.1	0.04	−0.2	−0.06

Discussion

The results show a great improvement in the quantitative character of the precipitation of WO_3, in comparison with the use of acids alone: all the methods have a good precision. However, some of these reagents, such as phenazone, tannin, tannin + phenazone, benzidine, *o*-tolidine and rhodamine B, are less satisfactory. They give an error higher than 0.6%, indicating a loss of WO_3 in all procedures. On the other hand, the precision and the accuracy of the methods using cinchonine or β-naphthoquinoline are excellent, the error being lower than 0.1%. Only these two methods can be recommended for the gravimetric determination of tungsten, as WO_3, from tungstate solutions.

SUMMARY

A comparison is made between gravimetric methods for the determination of tungsten from tungstate solutions. Precipitation of Hg_2WO_4 with $Hg_2(NO_3)_2$ in ammoniacal medium is used as reference method.

Precipitation of WO_3 with acids, followed by digestion, gives no quantitative results: the best method, using $HClO_4$, still gives rise to a negative error larger than 1%.

A survey of the organic reagents is given: of these, tannin is unsatisfactory (1.2%). Better results are obtained using benzidine (0.86%), *o*-tolidine (0.78%), phenazone (0.77%) and rhodamine B (0.70%). Only cinchonine (0.09%) and β-naphthoquinoline (0.06%) are to be recommended for the quantitative determination of tungsten from tungstate solutions.

RÉSUMÉ

Parmi les méthodes gravimétriques pour le dosage du tungstène, une première consiste à former le WO_3 et à digérer le précipité en présence d'une série d'acides. Même avec la meilleure méthode, celle employant l'acide perchlorique, l'erreur négative est de plus de 1%.

Dans la méthode de référence, le tungstate de mercure est précipité à l'aide du nitrate de mercure, et transformé en WO_3 à 850°C.

Parmi les réactifs organiques, l'acide tannique ne donne pas satisfaction (1.2%). Les autres, comme la benzidine (0.86%), l'*o*-tolidine (0.78%), la phénazone (0.77%) et la rhodamine B (0.70%), montrent une nette amélioration. Pourtant, deux réactifs donnent des résultats quantitatifs: la cinchonine (0.09%) et la β-naphtoquinoline (0.06%), et peuvent être recommandés pour la détermination du tungstène.

ZUSAMMENFASSUNG

Ein Vergleich der verschiedenen gravimetrischen Methoden zur Bestimmung von Wolfram zeigt, dass bei Gebrauch von Säuren und nachfolgender Digestion, grosse Fehler auftreten, die selbst bei der besten Methode, mit Perchlorsäure, noch etwas mehr als 1% betragen.

Als Referenz-Methode wurde die Fällung von Hg_2WO_4 mit Hilfe von $Hg_2(NO_3)_2$ und nachfolgender Umsetzung in WO_3 durch Glühen bei 850°C, angewendet.

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Ausser mit Tannin (1.2%), tritt mit organischen Reagenzien wie Benzidin (0.86%), *o*-Tolidin (0.78%), Antipyrin (0.77%) und Rhodamin B (0.70%) eine merkbare Verbesserung ein. Zwei Reagenzien, Cinchonin (0.09%) und β-Naphtochinolin (0.06%) liefern sehr gute Resultate, und können deshalb zur quantitativen Bestimmung des Wolframs empfohlen werden.

REFERENCES

[1] P. JANNASCH AND W. BETGES, *Ber.*, 37 (1904) 2219.
[2] G. VON KNORRE, *Ber.*, 38 (1905) 783.
[3] G. VON KNORRE, *Z. anal. Chem.*, 47 (1908) 37.
[4] M. TSILIKIN, *Ber.*, 42 (1909) 1302.
[5] M. NIERENSTEIN, *Analyst*, 50 (1925) 604.
[6] W. R. SCHOELLER, *Analyst*, 52 (1927) 702.
[7] L. MOSER AND J. SINGER, *Monatsh. Chem.*, 48 (1927) 673.
[8] L. MOSER AND F. LIST, *Monatsh. Chem.*, 51 (1929) 189.
[9] L. MOSER AND W. BLAUSTEIN, *Monatsh. Chem.*, 52 (1929) 351.
[10] W. R. SCHOELLER AND C. JAHN, *Analyst*, 52 (1927) 504; 59 (1934) 465.
[11] D. A. LAMBIE, *Analyst*, 64 (1939) 481; 68 (1943) 74; 70 (1945) 124.
[12] H. E. PETERSEN AND W. L. ANDERSEN, *U.S. Bur. Mines, Rept. Invest.*, No. 3709 (1943).
[13] S. H. WILSON AND M. FIELDES, *Analyst*, 69 (1944) 12.
[14] E. KAFKA, *Z. anal. Chem.*, 52 (1913) 601.
[15] A. GUTBIER AND G. L. WEISE, *Z. anal. Chem.*, 53 (1914) 426.
[16] G. DOTREPPE, *Bull. soc. chim. Belges*, 38 (1929) 375; 38 (1929) 385.
[17] J. H. YOE, *J. Am. Chem. Soc.*, 54 (1932) 1022.
[18] H. B. KNOWLES, *Bur. Standards, J. Research*, 9 (1932) 1.
[19] F. FEIGL, *Ind. Eng. Chem., Anal. Ed.*, 8 (1936) 401.
[20] R. BERG, *Die analytische Verwendung von o-Oxychinolin ,,Oxin'' und seiner Derivate*, 2nd Ed., Ferd. Enke Verl., Stuttgart, 1938.
[21] V. HOVORKA, *Collection Czech. Chem. Commun.*, 10 (1938) 518.
[22] J. LEFORT, *Z. anal. Chem.*, 21 (1882) 566.
[23] F. CREMER, *Eng. Mining J.*, 59 (1895) 345.
[24] A. H. LOW, *Eng. Mining J.*, 106 (1918) 47.
[25] F. G. ROHM, *Chem. and Met. Eng.*, 25 (1922) 1060.
[26] F. G. GERKE AND Z. I. KARDAKOVA, *Zavodskaya Lab.*, 6 (1937) 410.
[27] F. W. BOX, *Analyst*, 69 (1944) 272.
[28] B. A. PLATUNOV AND M. N. KIRILLOVA, *Khim. Referat. Zhur.*, 4 (1941) 73.
[29] J. T. OATS, *Eng. Mining J.*, 144 (1943) 72.
[30] C. SCHEIBLER, *J. prakt. Chem.*, 83 (1861) 273.
[31] C. DUVAL, *Anal. Chim. Acta*, 5 (1951) 401.
[32] J. J. BERZELIUS, *Schweigger's Journ.*, 16 (1816) 476; *Jahresber.*, 21 (1842) II, 143.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS. PART I

by

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Those who have to deal with the problems of qualitative analysis cannot but be aware of three defects in the various schemes for the detection of acids given in the current textbooks. The first is the absence of a systematic scheme of the type which is available for the detection of basic radicles, *i.e.* one in which the acidic constituents are precipitated in different groups by the addition of various group reagents and the precipitates thus obtained analysed systematically for the members of those groups. The second is the exclusion of a number of acids, which are well known and are in common use, from systematic analysis. Thus, there does not appear any justification for not including acids like phosphite, hypophosphite, bromate, iodate, periodate etc. in the systematic examination for acids. The third is the absence of any provision for detecting many elements in their acid forms. These elements, especially the so-called rare elements are generally present in the form of anions such as tellurite, tellurate, selenite, selenate, molybdate, etc. and it should be possible to detect these elements as such. If this is done, a clearer picture will be obtained with regard to the composition of the mixture.

Careful and detailed investigations have been carried out in this laboratory for some time with a view to devise a systematic scheme which is free from these defects. The results obtained are quite satisfactory and are embodied in the following series of papers. It is hoped that it will be possible to include other acidic constituents in the proposed scheme without altering its main outline.

The chief difficulty in the way of devising a scheme for the systematic detection of acids in solution is due to the fact that a large number of free acids are volatile or unstable. When an attempt is made to dissolve the mixture in acids, they either escape in the form of volatile products or are decomposed, chiefly due to mutual oxidation-reduction. Besides this, the salts formed by different acids with many basic radicles are frequently soluble in acids, and it is, therefore, not possible to use these basic radicles as group reagents in separating the acids from one another.

In view of the above-mentioned difficulties, efforts in this laboratory were confined to investigations in which the separations by group reagents were always made in an alkaline medium. The acids and their salts with bases generally show the maximum stability and the minimum solubility under these conditions. The sodium carbonate extract, which is generally prepared for the detection of anions, was considered to be the most suitable medium for separating acids into groups, not only because it provided a solution with mild alkaline properties, but also because the treatment with sodium carbonate precipitates a large number of basic radicles as hydroxides and carbonates and avoids their interference in the detection of the acids in the filtrate.

There were three problems to be solved before the sodium carbonate filtrate could be used for the systematic separation of acid radicles into groups by the addition of basic group reagents and their detection in the detailed analysis of each group: (a) the mutual oxidation-reduction of acids in alkaline solutions; (b) the solution of many elements in the sodium carbonate extract owing to their tendency to form amphoteric hydroxides or complexes; (c) the decomposition of certain acids in presence of sodium carbonate with the formation of other acids. Many acids interact with one another owing to mutual oxidation-reduction and thus one or the other disappears partly or completely on boiling the mixture with the sodium carbonate. It is true that the possibility of such reactions is reduced to the minimum in alkaline solutions as compared with acid solutions, but still some reactions do take place even in the mildly alkaline solution of sodium carbonate. An analyst must have a detailed knowledge of the behaviour of acids in this manner so that he may not only be on guard against missing certain acids owing to their decomposition or transformation by oxidation-reduction, but may also provide for their detection, if possible, by other methods. It is well-known that the following pairs of acids interact completely with each other in the presence of sodium carbonate and so one or the other will disappear from the solution according to the relative amount of the two present in the original mixture:

$$
\begin{gathered}
AsO_3^{-3} + IO_4^-;\ AsO_3^{-3} + Fe(CN)_6^{-3};\ AsO_3^{-3} + MnO_4^-;\ I^- + IO_3^-; \\
AsO_3^{-3} + CrO_4^{-2};\ I^- + IO_4^-;\ I^- + Fe(CN)_6^{-3};\ SO_3^{-2} + MnO_4^-; \\
I^- + MnO_4^-;\ PO_3^{-3} + MnO_4^-;\ PO_2^{-2} + MnO_4^-;\ IO_4^- + S^{-2};\ IO_3^- + S^{-2}; \\
BrO_3^- + S^{-2};\ IO_4^- + Fe(CN)_6^{-4};\ Fe(CN_6)^{-3} + S^{-2};\ MnO_4^- + S^{-2}; \\
CrO_4^{-2} + S^{-2};\ Fe(CN)_6^{-3} + S_2O_3^{-2};\ S_2O_3^{-2} + MnO_4^-; \\
TeO_3^{-2} + MnO_4^-;\ SeO_3^{-2} + MnO_4^-.
\end{gathered}
$$

In the case of iodide and ferricyanide, the reaction is rather slow and so both of the reacting acid constituents may be present simultaneously in the sodium carbonate filtrate. The mutual oxidation and reduction of iodide and iodate takes place very slowly in neutral medium but not in the presence of sodium carbonate. The problem of detecting acids which undergo oxidation-reduction in neutral or alkaline solution is under investigation, but this will not involve any change in the general procedure.

The second difficulty which is due to the amphoteric character of certain basic hydroxides or the formation of complexes leads to the contamination of the sodium carbonate filtrate with a fairly large number of basic constituents. Thus, hydroxides of metals like aluminium, beryllium, tin, etc., dissolve partially owing to the amphoteric character of their hydroxides; metals like nickel, cobalt, copper, etc., dissolve owing to the formation of complexes with ammonia, and metals like thorium, zirconium and uranium dissolve owing to the formation of complexes with sodium carbonate. These basic constituents are likely to interfere with the detection of the acid radicles, both in the separation of acids into groups and their detection in detailed analysis of the groups. Though the number of basic radicles which pass into the sodium carbonate filtrate is fairly large and might thus be expected to cause serious difficulties in devising a systematic scheme, actual investigations showed that the interference by these basic radicles was not as serious as could be expected. Most of these basic radicles get precipitated with zinc in the first group and cause hardly any further interference in the subsequent groups. It was also found that, inspite of the presence of a large number of basic radicles in the zinc group precipitate, the detection of the acids in this group could be carried out quite satisfactorily.

The third problem of the decomposition of certain acids with the formation of other acids on boiling with sodium carbonate is not serious. There are only two cases to be considered: the decomposition of hypochlorite into chloride and chlorate and that of phosphite into phosphate. The decomposition of phosphite takes place slowly in solutions of sodium carbonate, but rapidly in presence of sodium hydroxide. The hypophosphite does not decompose to an appreciable extent in the presence of sodium carbonate, although it decomposes rapidly in the presence of sodium hydroxide.

The general scheme proposed for the systematic detection of the acids in solution may be outlined as follows. The mixture containing all the constituents is boiled with sodium carbonate solution and any precipitate obtained is filtered off. The filtrate containing most of the acid radicles and some basic radicles is then treated with group reagents for their separation into groups. As has already been pointed out, the solution

TABLE I. SODIUM CARBONATE FILTRATE CONTAINING ALL THE ACIDS AND CERTAIN BASIC RADICLES

Treat with sufficient excess of $PbCO_3$ and filter

- Ppt.
  Lead salts of S^{-2}, VO_4^{-3}
- Filt.
  Rest of the acids
  Treat with $Zn(NO_3)_2$ or $Zn\ (CH_3COO)_2$, heat to boiling and filter
  - Ppt.
    Zinc salts of $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$, AsO_3^{-3}, AsO_4^{-3}, PO_3^{-3}, PO_4^{-3}, TeO_3^{-2}, TeO_4^{-2}, $B_4O_7^{-2}$, IO_4^-, (F^-), $C_2O_4^{-2}$ SeO_3^{-2}, (MoO_4^{-2}), (CrO_4^{-2}), WO_4^{-2}, SO_3^{-2}, SiO_3^{-2}, AlO_2^-, BeO_2^{-2}, SbO_3^{-3}, SbO_4^{-3}, SnO_2^{-2}, SnO_3^{-2} and U, Cu, Co, Ni, Zr and Th.
    Treat with excess of dil. NH_4OH and filter
    - Ppt.
      Zinc salts of $Fe(CN)_6^{-4}$, IO_4^-, TeO_4^{-2} and hydroxides of Zr^{+4}, Al^{+3}, Be^{+2}, Th^{+4} and PO_4^{-3}.
      See Table I, p. 373
    - Filt.
      $Fe(CN)_6^{-3}$, AsO_3^{-3}, AsO_4^{-3}, PO_3^{-3}, PO_4^{-3}, TeO_3^{-2}, (IO_4^-), (F^-), $C_2O_4^{-2}$, SeO_3^{-2}, MoO_4^{-2}, $B_4O_7^{-2}$, CrO_4^{-2}, SO_3^{-2}, WO_4^{-2}, SiO_3^{-2}, AlO_2^-, BeO_2^{-2}, SbO_3^{-2}, SbO_4^{-3}, SnO_2^{-2}, SnO_3^{-2} and complexes of U, Cu, Co and Ni.
      Add magnesia mixture and concentrated ammonia, heat and filter
      - Ppt.
        Magnesium salts of PO_3^{-3}, PO_4^{-3}, AsO_3^{-3}, AsO_4^{-3}, TeO_3^{-2}, (F^-), SiO_3^{-2}, AlO_2^-, BeO_2^{-2}, SnO_2^{-2}, SnO_3^{-2}, SbO_3^{-2}, SbO_4^{-3}.
        See Table II, p. 374
      - Filt.
        $Fe(CN)_6^{-3}$, (TeO_3^{-2}), (IO_4^-), $C_2O_4^{-2}$, CrO_4^{-2}, SeO_3^{-2}, SO_3^{-2}, $B_4O_7^{-2}$, MoO_4^{-2}, WO_4^{-2}, traces of Sb and Sn, and complexes of Cu, Co, Ni and U.
        Add $Ca(NO_3)_2$ and $Ba(NO_3)_2$, heat and filter
        - Ppt.
          Ba and Ca salts of (SeO_3^{-2}), MoO_4^{-2}, CrO_4^{-2}, $C_2O_4^{-2}$, WO_4^{-2}, SO_3^{-2}, TeO_3^{-2}, (IO_4^-) and BO_2^-.
        - Filt.
          $Fe(CN)_6^{-3}$, SeO_3^{-2}, BO_3^{-3}, and complexes of Co, Cu, Ni and U, and traces of Sb and Sn.

        See Table III, p. 375
  - Filt.
    $S_2O_3^{-2}$, CrO_4^{-2}, F^-, SeO_4^{-2}, IO_3^-, Cl^-, Br^-, I^-, SO_4^{-2}, MoO_4^{-2}, ClO_3^-, BrO_3^-, PO_2^{-2}, CNS^-, MnO_4^-, ClO_4^- and traces of Be, Co and Ni.
    Boil with excess of Na_2CO_3 and filter
    - Ppt.
      Carbonates of Zn, Ni and Co.
      Reject
    - Filt.
      $S_2O_3^{-2}$, MoO_4^{-2}, CrO_4^{-2}, SeO_4^{-2}, IO_3^-, F^-, Cl^-, Br^-, SO_4^{-2}, I^-, ClO_3^-, BrO_3^-, PO_2^{-2}, CNS^-, MnO_4^-, ClO_4^- (Be).
      Treat with $Cd(NO_3)_2$, heat and filter
      - Ppt.
        Cd salts of CO_3^{-2}, MoO_4^{-2}, IO_3^-, SeO_4^{-2} and CrO_4^{-2}.
        See Table IV, p. 376
      - Filt.
        F^-, (CrO_4^{-2}), (IO_3^-), Cl^-, Br^-, I^-, SO_4^{-2}, $S_2O_3^{-2}$, PO_2^{-2}, ClO_3^-, BrO_3^-, CNS^-, MnO_4^-, ClO_4^- and (Be) + Cd. Treat with $Ca(NO_3)_2$, heat to boiling and filter
        - Ppt.
          CaF_2.
        - Filt.
          SO_4^{-2}, CrO_4^{-2}, IO_3^-, Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, $S_2O_3^{-2}$, PO_2^{-2}, CNS^-, MnO_4^-, ClO_4^- and (Be).
          Add $Ba(NO_3)_2$ solution, heat to boiling and filter
          - Ppt.
            $BaSO_4$ and $BaCrO_4$.
          - Filt.
            IO_3^-, Cl^-, Br^-, I^-, ClO_3^-, BrO_3^-, $S_2O_3^{-2}$, PO_2^{-2}, CNS^-, MnO_4^-, ClO_4^- and (Be).
            Add $AgNO_3$, heat and filter
            - Ppt.
              Silver salts of Cl^-, Br^-, I^-, IO_3^-, CNS^-, PO_4^{-3} and S^{-2}.
            - Filt.
              ClO_4^-, ClO_3^-, BrO_3^-, PO_2^{-2} and MnO_4^-.

            See Table V, p. 377

is kept alkaline or neutral throughout the procedure for the separation of acids into groups to prevent the decomposition of certain acids or their interaction in other ways. Another reason for keeping the solution alkaline lies in the fact that the salts of the acids with many bases are more difficultly soluble in alkaline solution in comparison to neutral and acid solutions, and it becomes possible not only to precipitate them more completely but also to divide them into subgroups more easily. On account of the solubility of a very large number of salts in the presence of acids, separations in acid medium are of very limited scope and this has probably prevented the evolution of a satisfactory systematic scheme for the acid radicles so far. Separations of the acid radicles in alkaline solutions have made it possible to develop such a scheme and are probably the chief feature of the present scheme.

It will be seen that many of the elements which are generally detected in the systematic analysis for the basic radicles, will pass completely into the sodium carbonate filtrate and will be detected in the scheme for acid radicles. The detection of the basic constituents in the precipitate obtained on treatment with sodium carbonate will thus be simplified to a considerable extent. The number of acids which are not included in the systematic scheme and which have to be detected by other well-known methods is very small; these are acetate, nitrate, nitrite, carbonate, silicate and borate.

Although the use of organic reagents is fairly common, all tests included in the present scheme are of an inorganic nature to keep the scheme as simple as possible and widely applicable. A large number of mixtures were carefully analysed not only in the process of evolving the various parts of the scheme but also in testing the validity of the final scheme which is being put forward.

The separation of anions into different groups according to the new scheme may be represented diagrammatically as shown in Table I.

SUMMARY

A new and comprehensive scheme for the systematic detection of anions has been put forward. This scheme is based on the precipitation of difficultly soluble salts of anions in groups by basic group reagents in sodium carbonate solution and the subsequent analysis of each group precipitate or filtrate for the detection of individual members of the group.

RÉSUMÉ

Voici un schéma nouveau et très complet pour la détection systématique des anions: la méthode est basée sur la précipitation de sels peu solubles des anions, en groupes, par des réactifs spéciaux, en solution de carbonate de soude. Les composants de chacun des groupes sont ensuite détectés dans chaque groupe de précipités ou de filtrats.

ZUSAMMENFASSUNG

Ein neues und viel umfassendes Schema zum systematischen Nachweis der Anionen wird vorgeschlagen. Es gründet sich auf die Fällung schwerlöslicher Salze der Anionen in Gruppen mit Hilfe von Gruppenreagenzien in Natriumcarbonatlösung und die darauffolgende Analyse jeder Gruppe von Niederschlag und Filtrat zum Nachweis der einzelnen Anionen.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS. PART II

by

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In a previous paper[1] a comprehensive scheme for the systematic detection of anions has been proposed and the main outline of the scheme given.

In this paper the details of the procedures to be followed in separating the anions into various groups and detecting them systematically are given.

PROCEDURES

I. 2-3 g of the mixture is boiled with 8-10 g of sodium carbonate (AnalaR quality) and nearly 100 ml of water for about 10 minutes and then filtered. The filtrate will contain the sodium salts of practically all acids with the exception of certain acids, which form part of insoluble salts like sulphides of copper and zinc groups, silver halides, etc. It will also contain some basic radicles whose amphoteric hydroxides are soluble in alkaline solution or which form soluble complexes with ammonia or sodium carbonate.

II. The sodium carbonate filtrate is treated with sufficient excess of lead carbonate, boiled, cooled to room temperature and filtered. The precipitate with lead carbonate will contain sulphide and vanadate. The sulphides of arsenic, antimony and tin dissolve in sodium carbonate to give a mixture of thio- and oxythio salts. Lead carbonate converts thio- and oxythio-salts into oxy salts with the precipitation of lead sulphide. To ensure complete precipitation of vanadate as lead vanadate, a small portion of the filtrate is again shaken with lead carbonate and the washed precipitate is tested for vanadate by dissolving it in concentrated hydrochloric acid and adding hydrogen peroxide. If vanadate is found present, the whole filtrate is shaken with lead carbonate again and filtered. The precipitate is washed with distilled water and tested for sulphide and vanadate as usual.

III. The filtrate from procedure II is treated with a strong solution of zinc nitrate or acetate (about 1-2*M*) until no further precipitation takes place, boiled for 2-3 minutes and filtered. This will precipitate $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$, AsO_3^{-3}, AsO_4^{-3}, SeO_3^{-2}, WO_4^{-2}, TeO_3^{-2}, TeO_4^{-2}, SO_3^{-2}, IO_4^{-}, $C_2O_4^{-2}$, PO_3^{-3}, PO_4^{-3} and $B_4O_7^{-2}$ completely and F^-, MoO_4^{-2} and CrO_4^{-2} partially. In addition to these acids, all basic radicles which pass into the sodium carbonate filtrate are completely precipitated in this group, but nickel, cobalt and beryllium may be present in traces in the filtrate. The precipitate is washed 5-6 times with distilled water, only the first one or two washings being added to the main filtrate, the rest rejected to avoid increasing the volume unnecessarily.

The precipitate is divided into 3 sub-groups by adopting the following procedure.

(a) It is treated with excess of ammonium hydroxide, warmed and filtered after about 5 minutes. For satisfactory separation, the final strength of the ammonium hydroxide should be between 2-6*N*. The undissolved portion contains $Fe(CN)_6^{-4}$, TeO_4^{-2}, Zr^{+4} and Th^{+4} and portions of IO_4^{-}, Al^{+3} and Be^{+2}. As the phosphates of aluminium, beryllium, zirconium and thorium are insoluble in ammonium hydroxide, phosphate will also form part of the precipitate, if any of these four elements are present. The precipitate is washed first with 2*N* ammonium hydroxide to prevent salts which are soluble in ammonium hydroxide being reprecipitated, then with distilled water and analysed according to Table I.

(Text continued p. 378)

TABLE I

<table>
<tr><td colspan="7">Ppt.: Zinc salts of $Fe(CN)_6^{-4}$, IO_4^-, TeO_4^{-2}, hydroxides of Zr^{+4}, Al^{+3}, Be^{+2}, Th^{+4} and PO_4^{-3} if Zr etc. are present.
Treat with excess of NaOH solution and filter</td></tr>
<tr><td colspan="3">Ppt. Hydroxides and phosphates of Zr^{+4} and Th^{+4}. Treat with excess of dil. HNO_3 and filter</td><td colspan="4">Filt. $Fe(CN)_6^{-4}$, IO_4^-, PO_4^{-3}, TeO_4^{-2}, AlO_2^-, BeO_2^{-2}, ZnO_2^{-2}. Acidify with dilute HCl and filter</td></tr>
<tr><td rowspan="3">Ppt. White gelatinous zirconium phosphate</td><td colspan="2">Filt. Th^{+4}, PO_4^{-3} and Zr^{+4}; if PO_4^{-3} is absent $+HNO_3$.
(a) Test a portion for phosphate.
If PO_4^{-3} is present, test for Th only.
In case PO_4^{-3} is absent, add sodium phosphate to the rest of the solution, heat and filter after 10 min</td><td rowspan="3">Ppt. White $Zn_2Fe(CN)_6$ confirms $Fe(CN)_6^{-4}$</td><td colspan="3">Filt. IO_4^-, PO_4^{-3}, TeO_4^{-2}, Al^{+3}, Be^{+2} and Zn^{+2}.
(a) To a portion add conc. HCl and $FeSO_4$, warm and shake with CCl_4. Violet coloration in CCl_4-layer confirms IO_4^-.
(b) Concentrate the rest of the solution to a small volume, add conc. HCl, boil for 2-3 min (to reduce Te^{+6} to Te^{+4}). Treat with KI and Na_2SO_3. Dilute the solution, heat and filter</td></tr>
<tr><td rowspan="2">Ppt. White gelatinous zirconium phosphate confirms Zr</td><td rowspan="2">Filt. Th^{+4} and PO_4^{-3} $+HNO_3$. Add KIO_3 in excess.
White ppt. confirms Th</td><td rowspan="2">Ppt. Black Te(metal) confirms TeO_4^{-2}</td><td colspan="2">Filt. PO_4^{-3}, Al^{+3}, Be^{+2} and Zn^{+2}.
Treat with NH_4OH in excess and filter</td></tr>
<tr><td>Ppt. Hydroxides of Al^{+3}, Be^{+2} and PO_4^{-3}.
(i) Test a portion for PO_4^{-3}.
(ii) Test another portion for Al and Be with oxine as usual</td><td>Filt. Zn^{+2}.
Reject</td></tr>
</table>

TABLE II

<table>
<tr><td colspan="8">Ppt. Magnesium salts of AsO_3^{-3}, AsO_4^{-3}, PO_3^{-3}, PO_4^{-3}, TeO_3^{-2}, (F^-), SiO_3^{-2}, AlO_2^-, BeO_2^{-2}, SbO_4^{-3}, SbO_3^{-2}, SnO_2^{-2} and SnO_3^{-2}. Treat with dil. CH_3COOH till the solution is just acid. Further add equal volume of the acid to adjust its concentration at about 2*N*. Filter</td></tr>
<tr><td colspan="2" rowspan="2">Ppt. H_2TeO_3 and ($AlPO_4$). Dissolve the precipitate in dil. HCl, add Na_2SO_3, heat and filter.</td><td colspan="6">Filt. (F^-), AsO_3^{-3}, AsO_4^{-3}, PO_4^{-3}, PO_3^{-3}, SbO_4^{-3}, SbO_3^{-2}, SnO_2^{-2}, SnO_3^{-2}, (TeO_3^{-2}), SiO_3^{-2}, Al^{+3} and Be^{+2} + Mg^{+2}.
Add $Ca(NO_3)_2$ solution in slight excess, heat and filter</td></tr>
<tr><td rowspan="5">Ppt. White
CaF_2.
Confirm by SiF_4 test</td><td colspan="5">Filt. AsO_3^{-3}, AsO_4^{-3}, PO_3^{-3}, PO_4^{-3}, (TeO_3^{-2}), SbO_3^{-2}, SbO_4^{-3}, SnO_2^{-2}, SnO_3^{-2}, (SiO_3^{-2}), Al^{+3}, Be^{+2} + Mg^{+2} and Ca^{+2}
Add freshly prepared 1*N* Na_2S reagent[2] in excess and filter</td></tr>
<tr><td rowspan="4">Ppt. Black Te (metal) confirms **TeO_3^{-2}**</td><td rowspan="4">Filt. PO_4^{-3} and Al^{+3}. Test as usual</td><td rowspan="4">Ppt. PO_4^{-3}, PO_3^{-3}, Be^{+2}, Al^{+3} + Ca^{+2} and Mg^{+2}. Dissolve the precipitate in dil. CH_3COOH.
a) To a portion add $AgNO_3$ and warm. Immediate black precipitate confirms **PO_3^{-3}**.
b) If PO_3^{-3} is present, add dil. H_2SO_4 and Zn to the rest of the solution. Warm and keep aside for about 10 min (to decompose PO_3^{-3}). Test for PO_4^{-3} as usual.
In absence of PO_3^{-3}, PO_4^{-3} may be tested for directly.</td><td colspan="4">Filt. SiO_3^{+2}, thiosalts of AsO_3^{-3}, AsO_4^{-3}, (TeO_3^{-2}), SbO_3^{-2}, SbO_4^{-3}, SnO_2^{-2}, SnO_3^{-2}; (Al), (Be) + Ca and Mg.
Add equal volume of 2*N* HCl and filter</td></tr>
<tr><td colspan="3">Ppt. Sulphides of As^{+3}, Sb^{+3}, Sb^{+5}, Sn^{+2}, Sn^{+4} and Te^{+4}.
Boil with 6*N* HCl and filter</td><td rowspan="3">Filt. Thiosalt of AsO_4^{-3}, SiO_3^{-2}, (Al^{+3}), (Be^{+2}), + (Ca^{+2}) and (Mg^{+2}) Add conc. HCl in excess and boil. Yellow precipitate confirms **AsO_4^{-3}**</td></tr>
<tr><td colspan="2">Ppt. As_2S_3, TeS_2 and S. Dissolve in HCl and $KClO_3$.
Add KI and Na_2SO_3, dilute, heat and filter</td><td rowspan="2">Filt. Chlorides of Sb and Sn. Test as usual</td></tr>
<tr><td>Ppt. Black Te(metal) confirms **TeO_3^{-2}**</td><td>Filt. AsO_3^{-3}.
Add Na_2S, followed by an excess of conc. HCl and boil. Yellow precipitate Confirms **AsO_3^{-3}**</td></tr>
</table>

TABLE III

Filt Containing WO_4^{-2}, (TeO_3^{-2}), MoO_4^{-2}, CrO_4^{-2}, $C_2O_4^{-2}$, SO_3^{-2}, SeO_3^{-2}, IO_4^-, $B_4O_7^{-2}$, complexes of U, Cu and Ni, traces of Sb and Sn + Mg. Add $Ca(NO_3)_2$, $Fe(CN)_6^{-3}$ and $Ba(NO_3)_2$ solutions in slight excess, heat to boiling and filter

- Ppt. Ca and Ba salts of MoO_4^{-2}, WO_4^{-2}, CrO_4^{-2}, $C_2O_4^{-2}$, (TeO_3^{-2}), SO_3^{-2}, (SeO_3^{-2}), IO_4^- and BO_2^-. Treat with dil. CH_3COOH and filter
  - Ppt. Ca and Ba salts of MoO_4^{-2}, WO_4^{-2}, CrO_4^{-2}, $C_2O_4^{-2}$, (TeO_3^{-2}) and SO_3^{-2}. Boil with large excess of Na_2CO_3 solution and filter
    - Ppt. Carbonates of Ca and Ba. Reject
    - Filt. Sodium salts of MoO_4^{-2}, WO_4^{-2}, CrO_4^{-2}, $C_2O_4^{-2}$, (TeO_3^{-2}) and SO_3^{-2} + Na_2CO_3. Add excess of dil. CH_3COOH and $Ca(NO_3)_2$. Heat to boiling and filter
      - Ppt. CaC_2O_4 Confirm **$C_2O_4^{-2}$** as usual
      - Filt. MoO_4^{-2}, WO_4^{-2}, (TeO_3^{-2}), CrO_4^{-2}, SO_3^{-2} and Cr^{+3}, SO_4^{-2} if CrO_4^{-2} and SO_3^{-2} are present together. Add bromine water followed by excess of HCl, boil for 2-3 min and filter
        - Ppt. Yellow $WO_3 \cdot H_2O$. Confirm **WO_4^{-2}** as usual
        - Filt. SO_4^{-2}, MoO_4^{-2}, (TeO_4^{-2}), CrO_4^{-2} and Cr^{+3}. Add $Ba(NO_3)_2$ in slight excess, heat and filter
          - Ppt. $BaSO_4$. Confirms **SO_3^{-2}**
          - Filt. CrO_4^{-2}, Cr^{+3}, MoO_4^{-2} and (TeO_4^{-2}). Concentrate the solution to a small volume
1. To a portion add NaOH and Na_2O_2 and test for CrO_4^{-2}.
2. Add conc. HCl to the rest of the solution, boil for 2-3 min, add KI and Na_2SO_3, dilute, heat and filter
            - Ppt. Black Te(metal) Confirms **TeO_3^{-2}**
            - Filt. $MoCl_6$ and Cr^{+3}. Test as usual for **MoO_4^{-2}**
  - Filt. IO_4^-, SeO_3^{-2} and BO_2^-.
1. To a portion add conc. HCl and $FeSO_4$. Warm and shake with CCl_4. Violet coloration in CCl_4-layer confirms **IO_4^-**.
2. To the second portion add conc. HCl and thiourea. Heat to boiling. Red precipitate Se(metal) confirms **SeO_3^{-2}**
- Filt. $Fe(CN)_6^{-3}$, SeO_3^{-2}, complexes of U, Co, Cu, and Ni, and traces of Sb, Sn, BO_3^{-3} + Ca, Ba and Mg. Acidify with HCl, heat to boiling (to decompose the complexes of Cu, Ni and U), then add excess of NaOH heat (this decomposes the Co complex) and filter
  - Ppt. Hydroxides of Cu^{+2}, Co^{+2}, Ni^{+2}, $Na_2U_2O_7$ + Ca^{+2}, Ba^{+2} and Mg^{+2}. Dissolve in dil. HCl, add ammonium hydroxide in excess, heat to boiling and filter
    - Ppt. Yellow **$(NH_4)_2U_2O_7$**. Confirm as usual.
    - Filt. Cu^{+2}, Co^{+2} and Ni^{+2}. Test as usual
  - Filt. SeO_3^{-2}, $Fe(CN)_6^{-3}$, traces of Sb, Sn, BO_3^{-3} + Ca, Ba and Mg. Acidify the solution with HCl.
1. Test one portion for $Fe(CN)_6^{-3}$ with $FeSO_4$.
2. Test another portion for SeO_3^{-2} with thiourea

TABLE IV

Ppt. Cadmium salts of MoO_4^{-2}, SeO_4^{-2}, IO_3^- and CrO_4^{-2} + CO_3^{-2}. Boil with a large excess of Na_2CO_3 and filter				
Ppt. $CdCO_3$. Reject	Filt. Sodium salts of MoO_4^{-2}, SeO_4^{-2}, CrO_4^{-2} and IO_3^- + Na_2CO_3. Acidify with dil. CH_3COOH, add $Ba(NO_3)_2$ solution in slight excess, heat and filter			
	Ppt. Barium salts of MoO_4^{-2}, SeO_4^{-2} and CrO_4^{-2}. Dissolve the precipitate in conc. HCl. If the colour of the solution is yellow, shake it with ether and H_2O_2. Blue ethereal layer confirms **CrO_4^{-2}**. Reject the ethereal layer, neutralize the excess of acid in the aqueous portion with NaOH, add excess of Na_2S followed by equal volume of conc. HCl. Heat to boiling and filter			Filt. IO_3^- + Ba^{+2} and CH_3COOH. Add conc. HCl + $FeSO_4$. Shake with CCl_4. Violet coloration in CCl_4 layer confirms **IO_3^-**
	Ppt. Sulphides of Se and Mo. Dissolve in HCl and $KClO_3$. Add Na_2SO_3, heat and filter		Filt. Ba^{+2} and Cr^{+3}. Reject	
	Ppt. Red or black Se(metal) confirms **SeO_4^{-2}**	Filt. $MoCl_6$. Add KCNS and Zn. Blood-red colour confirms **MoO_4^{-2}**		

TABLE V

Filt. Containing IO_3^-, $S_2O_3^{-2}$, Cl^-, Br^-, I^-, CNS^-, ClO_3^-, BrO_3^-, ClO_4^-, MnO_4^-, PO_2^{-2}, (Be) + Cd, Ca and Ba.
Heat nearly to boiling and add $AgNO_3$ solution in slight excess. Filter and wash the precipitate with hot water

<table>
<tr>
<td colspan="4">Ppt. Silver salts of Cl^-, Br^-, I^-, CNS^-, IO_3^-, S^{-2} (from $S_2O_3^{-2}$) and (PO_4^{-3}) + Ag metal (due to PO_2^{-2}).
Treat a portion of the precipitate (in case black) with Zn and HCl.
Evolution of H_2S confirms $\mathbf{S_2O_3^{-2}}$.
Treat the precipitate with dil. HNO_3 and filter</td>
<td colspan="4">Filt. PO_2^{-2}, ClO_3^-, BrO_3^-, ClO_4^-, MnO_4^-, (Be^{+2}) + Ca^{+2}, Ba^{+2}, Cd^{+2} and Ag^+.
Heat the solution with slight excess of Na_2CO_3 and filter</td>
</tr>
<tr>
<td colspan="3">Ppt. Silver salts of Cl^-, Br^-, I^-, CNS^-, IO_3^- and Ag.
Treat with $1N$ NH_4OH and filter</td>
<td rowspan="3">Filt. (PO_4^{-3}).
Add ammonium and heat.
Yellow ppt. confirms $\mathbf{PO_2^{-2}}$</td>
<td rowspan="3">Ppt. Carbonates of Ca, Ba, Ag and Cd + Ag_2O.
Reject</td>
<td colspan="3">Filt. PO_2^{-2}, ClO_3^-, BrO_3^-, ClO_4^-, MnO_4^- and (Be^{+2}).
Concentrate the solution to about 20 ml and then add conc. HNO_3 to oxidize PO_2^{-2} to PO_4^{-3} completely.
Test a portion for PO_4^{-3}, if present.
The presence of PO_4^{-3} confirms $\mathbf{PO_2^{-2}}$.
Dilute the solution, add $NaNO_2$, heat (the pink colour of MnO_4^- will disappear, indicating the presence of $\mathbf{MnO_4^-}$), add $AgNO_3$ solution in slight excess and filter</td>
</tr>
<tr>
<td rowspan="2">Ppt. Silver salts of (Cl^-), Br^-, I^- and (CNS^-).
Test as usual</td>
<td colspan="2">Filt. IO_3^-, CNS^-, Cl^- + Ag^+ NH_4OH.
Add Na_2S and filter</td>
<td rowspan="2">Ppt. AgCl and AgBr.
Test as usual for Cl^- and Br^-.
Presence of Cl^- confirms $\mathbf{ClO_3^-}$ and that of Br^-, $\mathbf{BrO_3^-}$</td>
<td colspan="2">Filt. PO_4^{-3}, ClO_4^-, (Be^{+2}) and Mn^{+2} + Ag^+.
Neutralize the acid with NaOH, add slight excess of Na_2S (to remove Ag) and filter</td>
</tr>
<tr>
<td>Ppt. Ag_2S.
Reject</td>
<td>Filt. Ammonium salts of I^- (due to reduction of IO_3^-), CNS^- and Cl^-.
Test as usual.
The presence of iodide confirms $\mathbf{IO_3^-}$</td>
<td>Ppt. Ag_2S, MnS and $Be(OH)_2$.
Reject</td>
<td>Filt. ClO_4^- + Na_2S.
Acidify [illegible] O_4 and heat to boiling to remove H_2S. Filter off precipated sulphur.
Concentrate to about 5 ml, add excess of titanous sulphate, heat to boiling, add conc. HNO_3 to oxidize Ti^{+3} to Ti^{+4}.
Add $AgNO_3$ solution.
White precipitate AgCl confirms $\mathbf{ClO_4^-}$</td>
</tr>
</table>

(b) The ammoniacal filtrate from sub-group (a) is treated with magnesia mixture in slight excess and about 10 ml of concentrated ammonia is added to precipitate arsenite completely. It is heated nearly to boiling and filtered after 5-10 minutes. The precipitate will contain magnesium salts of AsO_3^{-3}, AsO_4^{-3}, PO_3^{-3}, PO_4^{-3}, (F^-), TeO_3^{-2}, SiO_3^{-2}, SnO_2^{-2}, SnO_3^{-2}, SbO_3^{-2}, SbO_4^{-3}, AlO_2^- and BeO_2^{-2}.

The precipitate is washed with $2N$ ammonium hydroxide and analysed according to Table II.

(c) The ammoniacal filtrate from sub-group (b) is treated with excess of barium and calcium nitrate solutions, heated nearly to boiling and filtered. The precipitate contains the calcium and barium salts of CrO_4^{-2}, (SeO_3^{-2}), IO_4^-, WO_4^{-2}, $C_2O_4^{-2}$, BO_2^-, MoO_4^{-2}, TeO_3^{-2} and SO_3^{-2} and the filtrate soluble salts of $Fe(CN)_6^{-3}$ and SeO_3^{-2}, complexes of uranium, cobalt, copper and nickel and traces of antimony, tin and borate. The precipitate and the filtrate are analysed according to Table III.

Traces of antimony and tin need not be tested for here, since these elements will be found practically *in toto* in the precipitate with magnesia mixture.

IV. Excess of zinc from the filtrate of procedure III is removed by adding slight excess of sodium carbonate which also renders the medium alkaline and prevents the interaction of various acid radicles on heating. The alkaline solution is concentrated to about 25 ml, treated with $0.5M$ cadmium nitrate solution in slight excess (iodate is not completely precipitated in the presence of large excess of cadmium nitrate), heated to boiling, cooled to room temperature and filtered. The precipitate will contain cadmium salts of CO_3^{-2}, MoO_4^{-2}, SeO_4^{-2}, IO_3^- and CrO_4^{-2}, but traces of IO_3^-, and CrO_4^{-2} may pass into the filtrate. The precipitate is washed with water and analysed according to Table IV.

V. The neutral filtrate from procedure IV is treated with calcium nitrate solution, any precipitate of calcium fluoride is filtered off and tested for fluoride as usual.

The filtrate from calcium fluoride is treated with barium nitrate solution, heated to boiling to precipitate the total amount of sulphate and chromate and washed with hot water. The presence of sulphate in the precipitate is confirmed by treating it with concentrated hydrochloric acid. Bromate is not precipitated at all by barium nitrate from hot solutions, as reported by some authors[2], and a trace of precipitate obtained from very concentrated solutions of bromate passes into the filtrate completely on washing with hot water 2-3 times. Iodate will be present in the filtrate from procedure IV only in traces and so will not be precipitated by barium nitrate. Barium thiosulphate is not precipitated owing to its tendency to form supersaturated solution.

VI. The neutral filtrate from procedure V is treated with slight excess of silver nitrate solution and filtered. The precipitate will contain the silver salts of IO_3^-, S^{-2} (from $S_2O_3^{-2}$), Cl^-, Br^-, I^-, CNS^-, PO_4^{-3} and Ag (due to PO_2^{-2}) and the filtrate PO_2^{-2}, BrO_3^-, ClO_3^-, MnO_4^-, ClO_4^- and (Be^{+2}). The precipitate and the filtrate are analysed according to Table V.

Note : Elements introduced as group reagents are placed in the tables after a + sign.

SUMMARY

Procedures for the separation of anions into groups and the detailed analysis of groups are given.

RÉSUMÉ

On donne les procédés de séparation en groupes et l'analyse détaillée de chaque groupe.

ZUSAMMENFASSUNG

Verfahren zur Trennung der Anionen in Gruppen und zur eingehenden Analyse dieser Gruppen werden vorgeschlagen.

REFERENCES

[1] I. K. Taimni and Manohar Lal, *Anal. Chim. Acta*, 17 (1957) 367.
[2] Ch. Malen and P. Bévillard, *Anal. Chim. Acta*, 8 (1953) 493.
[3] I. K. Taimni and G. B. S. Salaria, *Anal. Chim. Acta*, 13 (1955) 28.

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VOLUMETRIC ESTIMATION OF PERSULPHATE USING ARSENITE AS A PRIMARY STANDARD

by

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During the study of some reactions involving persulphate ion, difficulty was experienced in estimating the persulphate left over at different intervals of time, as there is no quick and direct method of titration. A study of these oxidation reactions led to the present investigation.

One of the possible methods for the estimation of the persulphate has been to decompose it to sulphate and estimate the sulphate as barium sulphate. This method, though giving the amount of sulphur present, fails to estimate the oxidant *i.e.*, persulphate present in the system. The second method of estimation involves the catalytic oxidation of certain reducing agents. In one[1] of these, excess of oxalic acid is added to the persulphate with a small amount of silver sulphate when oxalic acid is oxidized in presence of silver ions. The unused oxalic acid is then estimated by standard permanganate. In the other method[2] excess of ferrous ammonium sulphate is added to the persulphate, followed by the addition of hot water and the unoxidized ferrous sulphate is determined by the standard permanganate solution. Both of these methods are indirect ones, involving a second standard. The latter has additional disadvantage in using Bunsen valve to exclude any atmospheric oxidation of ferrous sulphate.

Yet another method has been suggested by BRIGHT AND LARABEC[3] and modified by SANDELL AND KOLTHOFF[4] in which Mn(II) is oxidized to permanganate by persulphate in hot acid solution in presence of silver ions. Permanganate so formed is estimated by sodium arsenite. SANDELL AND KOLTHOFF suggested the use of a mixture of sodium arsenite and sodium nitrite instead of arsenite alone. Prior precipitation of silver as a chloride is also necessary for accurate determination.

GOPALA RAO and co-workers[5] have estimated the persulphate by liberating the iodine catalytically from potassium iodide and determining the latter by a standard thiosulphate solution. The catalysts used were ferrous sulphate and cuprous iodide. The persulphate, potassium iodide and the catalyst had to be kept together for some time for completion of the reaction. This method was not found to be suitable in our case because besides being time consuming, the results obtained appear to be 1 to 2% too high.

In the present method, the persulphate solution is taken in the burette and the titration mixture consists of standard arsenious oxide solution with an excess of potassium iodide. The mixture is heated almost to boiling (about 80°C), some solid sodium bicarbonate is added and the persulphate is run in from the burette. The iodine liberated from the potassium iodide by the persulphate is instantaneously consumed by the arsenite solution. At the end-point, when all the oxide has been used up, the excess of persulphate liberates iodine and the colour of the solution becomes light yellow. Both free arsenious acid and neutral sodium arsenite were found to be suitable.

It was not possible to use starch here to mark the end-point, as the solution is hot.

EXPERIMENTAL PROCEDURE

The arsenious oxide, potassium persulphate and sodium bicarbonate used were all of B.D.H.A.R. quality. Potassium iodide was of pure E. Merck grade. The iodine used was of May & Baker resublimed quality. A 5 ml microburette was used and the 5 ml pipette was first standardized by the microburette. All the measuring flasks were standard ones.

A standard solution of *N*/5 arsenious oxide in the form of sodium arsenite was prepared in the same way as for iodometric estimation. *N*/10, *N*/20 and other solutions were prepared from this by dilution.

Arsenious acid was prepared by boiling the oxide (sufficient to give *N*/10 solution) with distilled water. The solution was allowed to cool and filtered. This was standardized with the aid of standardized iodine solution.

Persulphate solutions were always freshly prepared by direct weighing and the concentrations were checked by standard methods.

Preliminary experiments showed that the minimum concentration of potassium iodide should be 1*N* in the final solution. It should be mentioned that the liberation of iodine from potassium iodide by persulphate depends upon the concentration of both. Normal concentration or more of KI, at the end-point, is suitable to produce yellow colour even with 0.01 ml of persulphate of the concentrations used.

Five cc arsenite solution or free arsenious acid were taken in a 100 ml conical flask and 10 ml of 50% KI (approximately 3*N*) were added. The flask was heated almost to boiling (about 80°C). Then 2 g of sodium bicarbonate were added and the persulphate from the burette was run in the flask with constant shaking of the latter to eliminate any chance of iodine accumulating in and escaping from the system. Appearance of yellow colour marked the end-point. The temperature at the end of the titration was between 60-50°C. The readings were usually concurrent and the average of a number of observations was taken. Table I shows a set of typical results.

TABLE I

CONCENTRATION OF Na_3AsO_3 $49.80\cdot 10^{-3}$, CONCENTRATION OF $K_2S_2O_8$ $50.023\cdot 10^{-3}$, BLANK READING 0.01 ml OF PERSULPHATE

No.	*Volume of Na_3AsO_3* *ml*	*Volume of $K_2S_2O_8$ required* *ml*	*Volume of $K_2S_2O_8$ taken for calculation, after deducting the blank reading* *ml*	*Concentration of persulphate found* *N*	*Error* %
1	5	4.98	$4.98 - 0.01 = 4.97$	$\frac{49.80\cdot 10^{-3}\cdot 5}{4.97} = 50.1006\cdot 10^{-3}$	+ 0.16
2	5	4.97			
3	5	4.98			
4	5	4.99			
5	5	4.98			
6	5	4.98			

Some of the observations using different concentrations of the reactants are shown in Tables II and III.

DISCUSSION

It has been found that the percentage error in most cases is ± 0.20 and this is the maximum accuracy which can be achieved with a 5 ml microburette. Hence, the method can be recommended for a quick and direct determination of the persulphate. There is no difficulty in noting the end-point, especially when the persulphate solutions are

TABLE II

VOLUME OF H_3AsO_3 TAKEN 5 ml, BLANK READING 0.01 ml OF PERSULPHATE

No.	*Concentration of H_3AsO_3* N	*Concentration of $K_2S_2O_8$ taken* N	*Volume of $K_2S_2O_8$ required for 5 ml of H_3AsO_3, after deducting the blank reading* ml	*Concentration of $K_2S_2O_8$ founs* N	*Error* %
1	$99.19 \cdot 10^{-3}$	$50.023 \cdot 10^{-3}$	9.88	$50.174 \cdot 10^{-3}$	+ 0.34
2	$49.92 \cdot 10^{-3}$	$100.00 \cdot 10^{-3}$	2.485	$100.44 \cdot 10^{-3}$	+ 0.44
3	$49.92 \cdot 10^{-3}$	$50.023 \cdot 10^{-3}$	4.97	$50.22 \cdot 10^{-3}$	+ 0.40
4	$49.92 \cdot 10^{-3}$	$25.045 \cdot 10^{-3}$	9.935	$25.13 \cdot 10^{-3}$	+ 0.34
5	$24.90 \cdot 10^{-3}$	$50.023 \cdot 10^{-3}$	2.49	$50.00 \cdot 10^{-3}$	— 0.04
6	$24.90 \cdot 10^{-3}$	$25.045 \cdot 10^{-3}$	4.965	$25.08 \cdot 10^{-3}$	+ 0.16
7	$24.90 \cdot 10^{-3}$	$12.563 \cdot 10^{-3}$	9.90	$12.565 \cdot 10^{-3}$	— 0.01
8	$12.51 \cdot 10^{-3}$	$25.045 \cdot 10^{-3}$	2.495	$25.07 \cdot 10^{-3}$	+ 0.10
9	$12.51 \cdot 10^{-3}$	$12.563 \cdot 10^{-3}$	4.975	$12.57 \cdot 10^{-3}$	+ 0.05

TABLE III

VOLUME OF Na_3AsO_3 TAKEN 5 ml, BLANK READING 0.01 ml OF PERSULPHATE

No.	*Concentration of Na_3AsO_3* N	*Concentration of $K_2S_2O_8$ taken* N	*Volume of $K_2S_2O_8$ required for for 5 ml of Na_3AsO_3 after deducting the blank reading* ml	*Concentration of $K_2S_2O_8$ found* N	*Error* %
1	$199.5000 \cdot 10^{-3}$	$200.000 \cdot 10^{-3}$	4.97	$200.700 \cdot 10^{-3}$	+ 0.35
2	$199.500 \cdot 10^{-3}$	$100.000 \cdot 10^{-3}$	9.94	$100.35 \cdot 10^{-3}$	+ 0.35
3	$99.61 \cdot 10^{-3}$	$100.00 \cdot 10^{-3}$	4.965	$100.31 \cdot 10^{-3}$	+ 0.31
4	$99.61 \cdot 10^{-3}$	$200.00 \cdot 10^{-3}$	2.49	$200.02 \cdot 10^{-3}$	+ 0.01
5	$99.61 \cdot 10^{-3}$	$50.023 \cdot 10^{-3}$	9.94	$50.105 \cdot 10^{-3}$	+ 0.21
6	$49.80 \cdot 10^{-3}$	$100.00 \cdot 10^{-3}$	2.495	$99.79 \cdot 10^{-3}$	— 0.21
7	$49.80 \cdot 10^{-3}$	$50.023 \cdot 10^{-3}$	4.97	$50.100 \cdot 10^{-3}$	+ 0.16
8	$49.80 \cdot 10^{-3}$	$25.045 \cdot 10^{-3}$	9.935	$25.06 .10^{-3}$	+ 0.08
9	$24.90 \cdot 10^{-3}$	$50.023 \cdot 10^{-3}$	2.495	$49.89 \cdot 10^{-3}$	— 0.25
10	$24.90 \cdot 10^{-3}$	$25.045 \cdot 10^{-3}$	4.965	$25.08 \cdot 10^{-3}$	+ 0.16
11	$24.90 \cdot 10^{-3}$	$12.563 \cdot 10^{-3}$	9.935	$12.53 \cdot 10^{-3}$	— 0.24
12	$12.50 \cdot 10^{-3}$	$25.045 \cdot 10^{-3}$	2.495	$25.05 \cdot 10^{-3}$	+ 0.04
13	$12.500 \cdot 10^{-3}$	$12.563 \cdot 10^{-3}$	4.965	$12.580 \cdot 10^{-3}$	+ 0.20
14*	$6.25 \cdot 10^{-3}$	$6.25 \cdot 10^{-3}$	5.01	$6.2375 \cdot 10^{-3}$	— 0.20
15**	$6.25 \cdot 10^{-3}$	$3.125 \cdot 10^{-3}$	10.01	$3.1218 \cdot 10^{-3}$	— 0.10
16*	$3.125 \cdot 10^{-3}$	$6.250 \cdot 10^{-3}$	2.51	$6.225 \cdot 10^{-3}$	— 0.40
17**	$3.125 \cdot 10^{-3}$	$3.125 \cdot 10^{-3}$	5.01	$3.1187 \cdot 10^{-3}$	— 0.20
18***	$3.125 \cdot 10^{-3}$	$1.5625 \cdot 10^{-3}$	10.01	$1.5609 \cdot 10^{-3}$	— 0.10
19**	$1.5625 \cdot 10^{-3}$	$3.125 \cdot 10^{-3}$	2.49	$3.1375 \cdot 10^{-3}$	+ 0.40
20***	$1.5625 \cdot 10^{-3}$	$1.5625 \cdot 10^{-3}$	5.01	$1.5593 \cdot 10^{-3}$	— 0.20

* Blank reading was 0.02 ml of persulphate
** Blank reading was 0.03 ml of persulphate
*** Blank reading was 0.04 ml of persulphate

concentrated. Of course with very dilute solutions of persulphate of the order of 2 to $5 \cdot 10^{-3} N$, the yellow colour is obtained only after the addition of 0.02 to 0.04 ml of persulphate and that too, is not intense and so the end-point is not quite sharp with very dilute solutions of persulphate. It is not because the method fails with very dilute solutions, but because a great care in visual observation is needed with more dilute solutions of persulphate. Ordinarily the end-point is quite sensitive up to the persulphate concentrations of the order of $10 \cdot 10^{-3} N$.

The titration involves two reactions. The first is between persulphate and potassium iodide which is slow. This is made instantaneous by increasing the concentration of potassium iodide and heating the solution. The second reaction, between iodine and arsenite, is reversible. This is rendered irreversible by the addition of sodium bicarbonate which removes the hydrogen iodide formed in the reaction (2).

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2 \quad \text{. . . . . (1)}$$

$$As_2O_3 + 2I_2 + 2H_2O \rightleftarrows As_2O_5 + 4HI \quad \text{. . . . . (2)}$$

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SUMMARY

The method of estimating the persulphate by direct titration using arsenious acid or sodium arsenite as a primary standard has been described. This method consists in taking a mixture of arsenious acid or sodium arsenite and an excess of potassium iodide in the titration mixture. The mixture is heated to 80°C and solid sodium bicarbonate is added. Persulphate solution is run in from a burette and the liberated iodine is instantaneously consumed by trivalent arsenic. At the end-point an excess drop of persulphate gives a yellow colour due to the liberated iodine remaining unreacted. The results are satisfactory and the error lies within permissible limits.

RÉSUMÉ

On décrit une méthode de titrage direct de l'anion persulfurique, utilisant l'acide arsénieux et l'arsénite de sodium. La méthode consiste à mélanger l'acide arsénieux et l'arsénite de soude à un excès d'iodure de potassium, à chauffer ce mélange à 80°C et à y ajouter du bicarbonate de soude solide. On y laisse couler le persulfate d'une burette et l'iode libéré est instantanément consommé par l'arsénic trivalent. A la fin, un excès de persulfite produit une coloration jaune due à l'iode libéré ne réagissant plus. Les résultats sont satisfaisants et l'erreur se maintient dans les limites admises.

ZUSAMMENFASSUNG

Eine Methode zur Bestimmung von Persulfat durch direkte Titration unter Verwendung von arseniger Säure oder Natriumarsenit wird beschrieben. Die Methode besteht darin, dass man die arsenige Säure oder das Natriumarsenit mit einem Überschuss an Kaliumjodid mischt, auf 80°C erhitzt und festes Natriumbicarbonat zufügt. Man lässt nun aus einer Bürette die Persulfatlösung zufliessen; das frei gewordene Jod wird augenblicklich durch dreiwertiges Arsen verbraucht. Am Endpunkt gibt ein überschüssiger Tropfen Persulfat eine gelbe Farbe, die von dem freigewordenen Jod, das nicht mehr reagiert, herrührt. Die Ergebnisse sind befriedigend und die Fehler liegen innerhalb zulässiger Grenzen.

REFERENCES

[1] F. P. TREADWELL AND W. T. HALL, *Analytical Chemistry*, Vol. 2, *Quantitative Analysis*, 9th Edition, John Wiley & Sons, Inc., New York.
[2] LE BLANK ECKARDT, *Chem. News*, 81 (1900) 38.
[3] H. A. BRIGHT AND C. P. LARABEC, *Bur. Standards J. Research*, 3 (1929) 573.
[4] E. B. SANDELL, I. M. KOLTHOFF AND J. J. LINGANE, *Ind. Eng. Chem., Anal. Ed.*, 7 (1935) 256.
[5] G. GOPALA RAO, J. V. S. RAMANJANEYULEN AND V. MADHUSUDHANA RAO, *Proc. Natl. Inst. Sci. India*, 11 (1945) 331; *ibid.*, 12 (1946) 277.

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DETERMINATION OF METHYL KETONES BY pH MEASUREMENT

by

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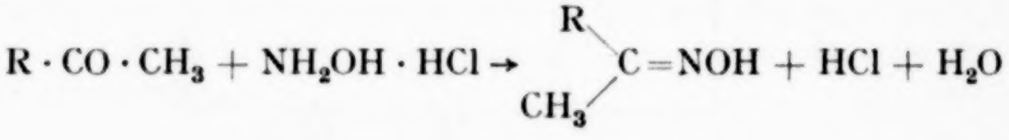
In a previous paper[1] it has been established that the iodoform reaction cannot be used for the quantitative estimation of methyl ketones. The bisulphite method[2] also gives low results.

Acetone and higher methyl ketones react with hydroxylamine hydrochloride and the reaction is expressed by the equation:



$$R \cdot CO \cdot CH_3 + NH_2OH \cdot HCl \rightarrow \begin{matrix} R \\ CH_3 \end{matrix}\!\!> C{=}NOH + HCl + H_2O$$

Titration of the free acid has been the basis for many methods of the analysis of carbonyl compounds[3]. For the quantitative estimation of acetone MARASCO[4] found an error of 5.5% and pointed out that oxime reaction is incomplete. However, MARASCO accounted for this factor by calibrating the method for each set of samples.

In this paper, the quantitative aspects are discussed of the hydroxylamine hydrochloride method for the determination of acetone and higher methyl ketones and it is established that the titration procedure gives invariably low results when used for the estimation of these ketones. However, the liberated acid causes a measureable drop in pH[5] and a rapid and accurate method is developed for the determination of methyl ketones which depends upon the calibration of a standard curve, a plot of known quantities of ketone *vs.* pH, for each set of samples. The concentration of the ketone from unknown sample may then be directly determined by pH measurement after oxime formation.

EXPERIMENTAL

Materials. The purest available commercial samples of the ketones were used. Acetone was further purified by the sodium iodide method[6]. The other ketones were dried (K_2CO_3) and then fractionated through a 1-meter column, the middle fractions of constant physical properties being retained. Hydroxylamine hydrochloride was of "AnalaR" purity.

All ketone solutions were prepared by weight according to GOODWIN's procedure[7] and were analysed by the hydroxylamine hydrochloride method.

Titration procedure. An 0.2% of the hydroxylamine hydrochloride containing five drops of screened methyl orange[8] was neutralized with 0.1*N* alkali to steel-grey colour. Two beakers, each containing 100 ml of neutralized hydroxylamine hydrochloride solution, were placed on a sheet of white paper; 25 ml of the ketone solution is added to one of the beakers, and the acid liberated was titrated with 0.1*N* sodium hydroxide till the colours in the two beakers were of equal intensity.

pH measurement. To 10 ml of 5% hydroxylamine hydrochloride solution in a 25 ml volumetric flask enough ketone solution was added to make the concentration after dilution not greater than 2.5 mg per ml. The resulting mixture was then diluted to 25 ml. After thorough mixing, the pH of the solution was measured with a pH meter and a standard curve was drawn. A typical curve for ethyl methyl ketone is shown in Fig. 1. The concentration of the ketone from unknown mixture is determined by measuring the pH after the oxime reaction. The range of sensitivity of the curve may be extended by varying the concentration of hydroxylamine hydrochloride.

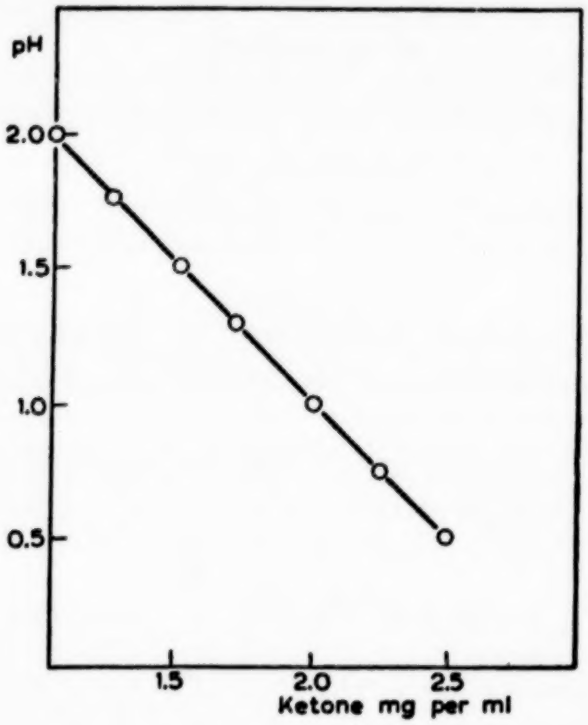


Fig. 1. Typical curve for ethyl methyl ketone.

In certain cases, where the reaction between ketone and hydroxylamine hydrochloride is slow, the reaction mixture was set aside for about two hours[9] for liberation of the free acid.

RESULTS

Some of the results obtained by the titration procedure are given in Table I. These show that the hydroxylamine titration method is not suitable for the quantitative estimation of these ketones, invariably giving low results.

TABLE I

UNRELIABILITY OF THE HYDROXYLAMINE TITRATION METHOD FOR QUANTITATIVE ANALYSIS OF METHYL KETONES

Ketone	*Concentration of solution (M)* *By weight*	 *By hydroxylamine method*	*Completion of the reaction* %
$CH_3 \cdot CO \cdot CH_3$	0.1083	0.1034	95.5
$CH_3 \cdot CH_2 \cdot CO \cdot CH_3$	0.1032	0.0951	92.2
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$	0.0348	0.0302	86.5
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 . CO \cdot CH_3$	0.0494	0.0417	84.4
$(CH_3)_2 \cdot CH \cdot CO \cdot CH_3$	0.0561	0.0475	84.8
$(CH_3)_3C \cdot CO \cdot CH_3$	0.0519	0.0238	45.8

In Table II are given some typical results obtained for the determination of some methyl ketones by pH measurement and it will be seen that these ketones can be determined accurately by this procedure.

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TABLE II

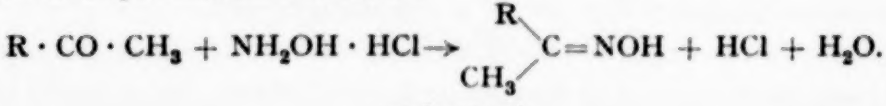
DETERMINATION OF METHYL KETONES BY pH MEASUREMENTS

Ketone	*Amount present* mg	*Amount found* mg
$CH_3 \cdot CO \cdot CH_3$	55.7	55.7
	43.4	43.4
	37.7	37.6
$CH_3 \cdot CH_2 \cdot CO \cdot CH_3$	60.4	60.4
	45.7	45.7
	39.9	39.9
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$	49.2	49.2
	44.6	44.6
	32.5	32.5
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$	47.6	47.6
	41.4	41.4
	35.9	35.9
$(CH_3)_2 \cdot CH \cdot CO \cdot CH_3$	63.4	63.4
	50.7	50.7
	35.3	35.2
$(CH_3)_3C \cdot CO \cdot CH_3$	49.4	49.3
	42.2	42.2
	33.7	33.7

The experiments were repeated with the addition of 2, 8 and 20% of ethyl alcohol in each set of experiments given in Table II and it was found that the presence of alcohol did not affect the results.

SUMMARY

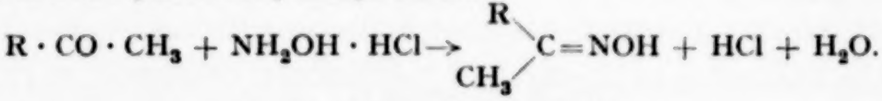
A rapid and accurate method for the determination of methyl ketones in presence of ethyl alcohol is described; it depends upon the measurement of pH after the liberation of free hydrochloric acid in the hydroxylamine hydrochloride reaction:



$$\mathrm{R\cdot CO\cdot CH_3 + NH_2OH\cdot HCl \rightarrow {}^{R}_{CH_3}\!\!>C{=}NOH + HCl + H_2O.}$$

RÉSUMÉ

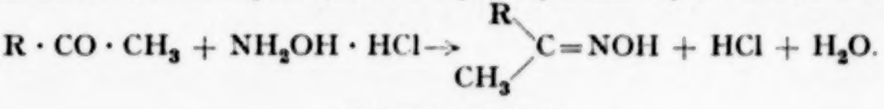
On décrit une méthode rapide et précise de détermination des méthyl-cétones en présence d'alcool éthylique. Elle repose sur la mesure du pH lors de la libération d'acide chlorhydrique dans la réaction des cétones avec le chlorhydrate d'hydroxylamine:



$$\mathrm{R\cdot CO\cdot CH_3 + NH_2OH\cdot HCl \rightarrow {}^{R}_{CH_3}\!\!>C{=}NOH + HCl + H_2O.}$$

ZUSAMMENFASSUNG

Eine rasche und genaue Methode zur Bestimmung der Methylketone in Gegenwart von Äthylalkohol wird beschrieben. Sie gründet sich auf die Messung des pH nach dem Freiwerden von Salzsäure bei der Reaktion der Methlyketone mit Hydroxylamin-Hydrochlorid nach der Gleichung:



$$\mathrm{R\cdot CO\cdot CH_3 + NH_2OH\cdot HCl \rightarrow {}^{R}_{CH_3}\!\!>C{=}NOH + HCl + H_2O.}$$

REFERENCES

1 C. F. CULLIS AND M. H. HASHMI, *J. Chem. Soc.*, (1956) 2512.

2 I. M. KOLTHOFF AND V. A. STENGER, *Volumetric Analysis*, Vol. II, Interscience Publishers, New York, 1947, p. 221.

3 K. HOEPNER, *Z. Untersuch. Nahr. u. Genussm.*, 34 (1917) 453.

4 M. MARASCO, *Ind. Eng. Chem.*, 18 (1926) 701.

5 R. E. BYRNE, *Anal. Chem.*, 20 (1948) 1245.

6 K. SHIPSEY AND E. A. WERNER, *J. Chem. Soc.*, 103 (1913) 1255.

7 L. F. GOODWIN, *J. Am. Chem. Soc.*, 42 (1920) 39.

8 K. C. D. HICKMAN AND R. P. LINSTEAD, *J. Chem. Soc.*, 121 (1922) 2502.

9 A. H. BENNETT AND F. K. DONOVAN, *Analyst*, 47 (1922) 146.

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THE DETERMINATION OF CHLORATES IN THE PRESENCE OF PERCHLORATES. REDUCTION OF CHLORATES IN ACID SOLUTION EMPLOYING EXCESS Fe(II) OR As(III)

by

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INTRODUCTION

Interest in the commercial production on a large scale of potassium and ammonium perchlorates for use as oxygen carriers in the manufacture of pyrotechnical compositions, solid rocket propellant fuels, and in the large scale production of perchloric acid ($HClO_4 \cdot 2H_2O$ or preferably oxonium perchlorate, $(OH_3)ClO_4 \cdot H_2O$, monohydrate) has increased rapidly within the last few years. This process depends upon the electrolytic oxidation of chloride to chlorate and subsequent oxidation to perchlorate. An outstanding characteristic of the electrolytic oxidation of sodium chloride to sodium chlorate, followed by the separate electro-oxidation of sodium chlorate to perchlorate, is that neither process requires the use of a diaphragm cell.

The oxidation of sodium chloride to chlorate involves the use of graphite anodes and iron cathodes. The second stage of oxidation utilizes platinum anodes and iron cathodes. In both cell oxidations, chromate is employed to prevent reduction of the anion at the surface of the iron cathode, the use of which would not be required in case nickel cathodes were employed.

The electro-oxidation is not carried to completion in either of the required two-stage oxidations. In the oxidation of chlorate to perchlorate, ordinarily carried to 97-98% completion, after which current efficiency rapidly falls off due to formation of ozone at the anode, there is required an analytical procedure in the determination of small amounts of chlorate in the presence of high concentrations of perchlorate.

The present objective is the study of this problem.

GENERAL REACTION CHARACTERISTICS

The proposed operation manipulations involve the reduction of acid solutions of the electro-oxidation cell electrolyte, consisting of large amounts of sodium perchlorate and minor concentrations of sodium chlorate, selectively. The reductant must be specific towards chloric acid and without reduction of perchloric acid under the proposed reaction of reduction.

The sluggish reduction of chloric acid in the presence of perchloric acid with well-suited standard reducing agents at ordinary temperatures demands that excess reductant be employed for a given time interval to be followed by a reverse quantitative oxidation of excess reductant to complete the analysis.

The specific reduction of the chlorate ion in the presence of perchlorate can be carried out employing either ferrous sulfate or arsenious acid. For short intervals of reduction time the controlling factors are pH, reductant excess, and the presence of a suitable catalyst. For the latter purpose osmic acid serves effectively. The excess of ferrous sulfate or arsenite is determined by use of standard sulfato-ceric acid with ferroine as reaction indicator. For this reaction osmic acid as catalyst is likewise essential. The well-known resistance of the perchlorate anion to reduction serves to prevent interference from excess reductants Fe(II) and As(III).

PREPARATION OF REAGENTS

Potassium chlorate. Reagent grade material was purified by recrystallization from dilute hydrochloric acid solution followed by centrifugal filtration and washing with drying at 50°C to constant weight. Recrystallized CAF Kahlbaum potassium chlorate or the Merck reagent grades by this process were estimated, following the method of determination to be described, to be pure to within 0.01-0.02% of theoretical.

Osmic acid catalyst. A solution $0.01 M$ in OsO_4 was prepared in $0.1 N$ sulfuric acid.

Other reagents. Reagent grade commercially available reagent acids were employed. A dilute solution of sulfuric acid 0.15-$0.25 N$ in ferrous sulfate served as one reductant. Approximately $0.25 N$ sulfato-ceric acid is best prepared by the dissolution of hydrated ceric oxide, $[Ce(OH)_4]$, in hot, dilute (1 + 3) reagent sulfuric acid and adjustment of the clear solution resulting to volume in preparation for standardization.

Standard ferrous sulfate and sulfato-ceric acid. The sulfato-ceric acid was standardized, employing standard of reference purity arsenious oxide in sulfuric acid solution with osmic acid as catalyst and ferroine as indicator. The ferrous sulfate was standardized by comparison with standard sulfato-ceric acid employing the same redox indicator.

ANALYTICAL PROCEDURE

A sample of electrolyte (50 ml) from the electro-oxidation of sodium chlorate to perchlorate containing 100-200 mg of chlorate and a proportionately large amount of perchlorate is pipetted into a 400 ml beaker. Sufficient sulfuric acid to make the solution $1 M$ in case arsenite reduction is to be applied, and $3 M$ in case ferrous sulfate is operative, is added. 0.1 ml of the osmic acid catalyst solution is then added, followed by a known volume of 0.1500 to $0.2500 N$ ferrous sulfate or arsenite as reductant. The solution is stirred and allowed to react during a 15 min interval. A drop of $0.025 N$ ferroine indicator is then added. The ferrous complex ferroine perchlorate will first form and will dissolve instantaneously upon stirring. The excess reductant is now titrated using 0.1000-$0.1500 N$ sulfato-ceric acid; the ferroine indicator red is immediately converted to a faint blue at the equivalent point upon addition of the first excessive drop. All reactions are carried out at room temperature. The number grams of chlorate per liter of cell electrolyte may be readily calculated from the excess of reductant.

TEST ACCURACY TITRATIONS FROM PURE $KClO_3$ TITRATIONS

Samples of pure potassium chlorate were weighed into 400 ml beakers and a large excess of reagent chlorate free sodium perchlorate monohydrate (or perchloric acid), was added and the solution adjusted to $1 M$ using sulfuric acid. A 0.1 ml of osmic acid catalyst was added, followed by a two-fold excess of standard sodium arsenite. After stirring, the reaction was allowed to continue in covered beakers for 15 minutes. Ferroine indicator was then added and the solutions back-titrated with the standard sulfato-ceric acid. Results from a series of analyses are given in Table I.

Upon addition of arsenite to the mixed perchlorates under these conditions, a momentary liberation chlorine is initially observed. This reaction product disappears in a matter of 2-3 minutes. It was not found necessary to carry out the reaction of chlorate reduction in a closed reaction flask.

Using approximately $1 N$ H_2SO_4 for a reduction period of three hours, but otherwise duplicating the conditions given in Table I, the results given in Table II were obtained.

TABLE I

DETERMINATION OF CHLORATE IN THE PRESENCE OF PERCHLORATE

Reductant: 50.00 ml of 0.2294*N* sodium arsenite. Reaction acidity: 1*M* in $H_2SO_4 + HClO_4$. Catalyst: 0.1 ml of 0.01*M* OsO_4. Perchloric acid added: 5.0 ml of 72% $HClO_4$. Oxidant: 0.10415*N* $H_2Ce(SO_4)_3$. Ferroine redox indicator. Room temperature: 25°C. Reaction time of reduction: 15 min. Volume during reduction was 100 ml.

Sample wt $NaClO_3$ *g*	*Ce(IV) added ml*	$NaClO_3$ *found g*	*Error g*
0.1624	22.30	0.1623	—0.0001
0.1509	28.55	0.1508	—0.0001
0.1730	16.68	0.1727	—0.0003
0.1464	31.00	0.1462	—0.0002
0.1584	24.70	0.1579	—0.0005
		Av.	—0.0002
		Av. error in %	—0.12

TABLE II

DETERMINATION OF CHLORATE IN THE PRESENCE OF PERCHLORATE

Reductant: 50.00 ml of 0.2717*N* sodium arsenite. Catalyst: 0.10 ml of 0.01*M* osmic acid in 0.1*N* H_2SO_4. Oxidant: 0.1147*N* sulfato-ceric acid. Acid concentration: 0.9*N* H_2SO_4. Reaction time: three hours.

Sample wt g	$H_2Ce(SO_4)_3$ *ml*	$KClO_3$ *calculated g*	*Error g*
0.2091(5)	29.23	0.2090	—0.0001(5)
0.2108	28.60	0.2105	—0.0003
0.2121	28.10	0.2116	—0.0005
0.2111	28.28	0.2112	+0.0001
		Av.	—0.0002
		Av. error in %	—0.09

For the procedure employed as outlined in Table II, the chlorate was dissolved in 50 ml of water, the mineral acid (aside from the free acid of the oxidant solution) required to fortify the solution was added; to provide test conditions of chlorate in the presence of perchlorate, the acid used was perchloric acid. The catalyst was then provided and the reaction mixture allowed to stand at room temperature during a period of three hours. Ferroine redox indicator was employed in the titration of excess arsenite.

TABLE III

DETERMINATION OF CHLORATE IN THE PRESENCE OF PERCHLORATE $FeSO_4$ AS REDUCTANT

Reaction temp. 25°C. Ferrous sulfate 0.2501(5)*N*, 50.00 ml

Sample wt g	*Acid Concn. N*	*Reaction time min*	$H_2Ce(SO_4)_3$ *taken N*	$H_2Ce(SO_4)_3$ *required ml*	$KClO_3$ *found g*	*Error mg*
0.2101(5)	2.0	100	0.1147	9.32	0.2102	+0.00(5)
0.2097	2.0	96	,,	19.57	0.2096	—0.01
0.2117	2.0	95	,,	18.72	0.2116	—0.01
0.2089	2.0	93	,,	19.86	0.2089	—0.00(5)
0.2096	2.0	87	,,	19.60	0.2095(5)	—0.00(5)
0.2027(5)	2.0	49	0.1141(5)	24.81	0.2027	0.00
0.2005	2.0	46	,,	25.90	0.2004	—0.01
0.2025	2.0	43	,,	24.95	0.2024	—0.01
0.2030(5)	2.0	42	,,	24.70	0.2029	—0.01(5)
0.2020	2.0	40	,,	25.17	0.2019	—0.01
0.2113	3.0	19	0.1147	19.80	0.2014	+0.01
0.2114	3.0	18	,,	18.85	0.2113	—0.01
0.2116	3.0	18	,,	18.78	0.2115	—0.01
0.2101	3.0	15	,,	19.65	0.2094	—0.07
					Av.	±0.01

TEST ANALYSES EMPLOYING FERROUS SULFATE AS REDUCTANT

The same procedures as described in the use of arsenite as reductant were duplicated, employing ferrous sulfate in place of arsenite. The same catalyst was used and the ferrous sulfate solution was 0.36*N* in sulfuric acid. Results from a series of analyses are given in Table III. Perchloric acid was used to adjust the acidity during chlorate reduction period.

From an examination of the data in Table III, it will be observed that the reaction of ferrous sulfate in the reduction of chlorate at room temperatures is pH controlled. In 2*N* sulfuric acid the reaction time is 40 minutes. In 3*N* H_2SO_4 the reaction time is 15-20 minutes. No oxidation by atmospheric oxygen upon excess Fe(II) was observed for the time intervals employed.

GENERAL CONCLUSIONS

Sodium arsenite and ferrous sulfate are suitable as reductants for chlorate in the presence of perchlorate, employing osmic acid as catalyst. The sulfuric acid concentration for rapid reduction by arsenite is *N*. For ferrous sulfate a concentration of 3*N* sulfuric acid is preferable. In both cases 15-20 minutes are suitable for complete reduction of chlorate. No need to exclude contact with atmospheric oxygen was found. Standard sulfato-ceric acid is suitable in both cases in the determination of excess reductant with ferroine as redox indicator. Since acid solutions of the perchlorate ion are not reduced by either Fe(II) or As(III), no interference from perchlorate was found.

SUMMARY

A procedure is given for the determination of moderate amounts of chlorate in the presence of large amounts of perchlorate. Two reductants, Fe(II) and As(III), were employed with reverse titration of excess reductant by standard sulfato-ceric acid. Osmic acid as catalyst is requisite. Ferroine redox indicator was employed. The influence of acid concentration, temperature, and reaction time was determined. The procedures described were applicable to the analysis of $NaClO_3$-$NaClO_4$ electro-oxidation cell electrolytes for determination of cell reaction completion.

RÉSUMÉ

Le dernier stade de la préparation du perchlorate consiste en une oxydation du chlorate par électrolyse. Le rendement de cette opération est de 97-98%. Pour contrôler ce rendement, il a été mis au point une méthode d'identification des chlorates en faible quantité, en présence d'une grande quantité de perchlorates. On emploie deux réducteurs, le Fe(II) et le As(III) dont on titre l'excès par l'acide sulfato-cérique standard. La ferroïne est utilisée comme indicateur rédox. On titre en milieu acide. Les conditions d'acidité, de température et de temps de réaction ont été déterminées.

ZUSAMMENFASSUNG

Die letzte Stufe der Herstellung von Perchlorat ist eine elektrolytische Oxydation des Chlorates. Die Ausbeute dieser Operation beträgt 97-98%. Um diese Ausbeute zu kontrollieren, wurde eine Methode zur Identifizierung kleiner Chloratmengen in Gegenwart grosser Perchloratmengen ausgearbeitet. Man verwendet zwei Reduktionsmittel, Fe(II) und As(III), und titriert deren Überschuss mit einer Standardlösung von Sulfato-Cersäure.

Ferroin dient als Redox-Indikator. Man titriert in saurer Lösung. Der Einfluss von Säuregrad, Temperatur und Reaktionsdauer wurde festgestellt.

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SEPARATIONS INVOLVING SULPHIDES

III. SEPARATION OF RHENIUM AND ANTIMONY FROM MERCURY

by

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In a previous paper[1] it has been shown that arsenic, molybdenum and tellurium can be successfully separated from mercury provided one portion of the solution containing the two metals is treated with an excess of the alkali sulphide reagent (the thiosalt of mercury decomposed with an excess of ammonium acetate at a low temperature) and another portion containing the two metals treated with hydrochloric acid to decompose both the thiosalts. It has been found that rhenium can also be separated from mercury by the same method, provided ammonium sulphate is added to complete the precipitation of rhenium heptasulphide with mercuric sulphide. In the case of antimony, a slight modification is necessary because the precipitate of mercuric sulphide formed in the presence of antimonate has a tendency to get peptized and low results are obtained for mercury. The thiosalts of the two metals have to be decomposed with different concentrations of hydrochloric acid in order to get satisfactory results. If antimony is determined in the filtrate from mercuric sulphide, high results are obtained owing to occlusion of sulphur.

EXPERIMENTAL

Separation of rhenium from mercury

Measured portions of standard solutions of mercuric chloride[2,3] (AnalaR quality) and potassium perrhenate[4] were mixed together. In one set of experiments, the solution was treated with 60-70 ml of 2*N* sodium sulphide reagent[5]; the thiosalt of mercury decomposed by adding an excess of ammonium acetate (solid) and mercury estimated as sulphide[2]. In another set of experiments, the mixture of the thiosalts was treated with a large excess of 12*N* hydrochloric acid followed by 10-15 g of ammonium sulphate (solid) to precipitate rhenium as heptasulphide completely. The precipitate of the mixed sulphides was weighed after suitable treatment[4] and the weight of precipitated rhenium heptasulphide determined by difference.

The results are given in Table I.

TABLE I

DETERMINATION OF RHENIUM AND MERCURY IN A MIXTURE WITH 2*N* SODIUM SULPHIDE REAGENT

Wt of Hg in HgS g	*Wt of Hg actually present* g	*Wt of Re in* Re_2S_7 g	*Wt of Re actually present* g
0.10600	0.10620	0.03089	0.03095
0.10600	0.10620	0.02477	0.02477
0.04242	0.04249	0.03089	0.03095

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Separation of antimony from mercury

Measured volumes of standard solutions of mercuric chloride[2,3] and potassium hydrogen antimonate[6] (E. Merck Guaranteed Reagent) were mixed together and treated with 60-70 ml of 2*N* sodium sulphide reagent[5]. In one set of experiments the mixture of the thiosalts was treated with a large excess of 12*N* hydrochloric acid, the concentration of the acid in the resulting mixture was adjusted at a little above 6*N* and the mixture heated to boiling to dissolve the precipitated antimony pentasulphide. The precipitate of mercuric sulphide was filtered through a weighed, sintered glass crucible (porosity 4), washed first with hot 6*N* hydrochloric acid and then thoroughly with distilled water, alcohol and ether successively, dried in an air-oven at 105°C for an hour and weighed. In another set of experiments, the mixture of the thiosalts formed with the alkali sulphide reagent was treated with a large enough excess of 2*N* hydrochloric acid to produce a concentration of 1*N*, the mixture was heated to boiling and allowed to cool to the room temperature. The precipitate of the mixed sulphides was weighed after suitable treatment[2] and the weight of the precipitated antimony pentasulphide was determined by difference.

The results are given in Table II.

TABLE II

DETERMINATION OF ANTIMONY AND MERCURY IN A MIXTURE WITH 2*N* SODIUM SULPHIDE REAGENT

Wt of Hg in Hgs g	*Wt of Hg actually present* g	*Wt of Sb in Sb_2S_5* g	*Wt of Sb actually present* g
0.07381	0.07394	0.02719	0.02726
0.07398	0.07394	0.05445	0.05449
0.07406	0.07394	0.05451	0.05449

Note on the separation of platinum, gold, selenium and tin from mercury

When solutions containing platinum, gold, selenium or tin in the presence of mercury are treated with an excess of the alkali sulphide reagent, a mixture of thiosalts is obtained which on treatment with ammonium acetate precipitates mercury as mercuric sulphide. The slow decomposition of the thiosalts of platinum, gold and selenium on exposure to air, or on standing, leads to the contamination of the precipitate of mercuric sulphide with these metals and makes the method inapplicable in quantitative separations. In the presence of tin, the precipitate of mercuric sulphide obtained by treating with sodium sulphide and ammonium acetate is not of the usual character and has a great tendency to peptize on washing with water. It also dissolves in 6*N* hydrochloric acid and thus the method used in separating mercury from antimony is not applicable.

SUMMARY

It has been shown that it is possible to estimate rhenium or antimony in the presence of mercury by decomposing their thiosalts but not platinum, gold, selenium and tin.

RÉSUMÉ

On démontre qu'il est possible de doser le rhénium et l'antimoine en présence de mercure en décomposant leurs thio-sels, mais non pas le platine, l'or, le sélénium et l'étain.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Rhenium und Antimon, nicht aber Platin, Gold, Selen und Zinn, in Gegenwart von Quecksilber durch Zersetzung ihrer Thiosalze bestimmt werden können.

REFERENCES

[1] G. B. S. Salaria, *Anal. Chim. Acta.*, 16 (1957) 3.
[2] G. B. S. Salaria, *ibid.*, 15 (1956) 515.
[3] I. K. Taimni and G. B. S. Salaria, *ibid.*, 12 (1955) 522.
[4] I. K. Taimni and G. B. S. Salaria, *ibid.*, 12 (1955) 519.
[5] I. K. Taimni and G. B. S. Salaria, *ibid.*, 13 (1955) 28.
[6] G. B. S. Salaria, *ibid.*, 17 (1957) 395.

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SEPARATIONS INVOLVING SULPHIDES

IV. SEPARATION OF PLATINUM, GOLD, SELENIUM, ARSENIC, RHENIUM AND MOLYBDENUM FROM LEAD

by

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In earlier publications[1,2] separations of some metals of the arsenic group from mercury were dealt with. In this paper methods for the separation of platinum, gold, selenium, arsenic, rhenium and molybdenum from lead are proposed.

EXPERIMENTAL

Separation of platinum from lead

Measured volumes of the standard solutions of lead acetate[3] (prepared with acetic acid) and platinic chloride[4] were mixed togehter; the free acid was neutralized with 8*N* sodium hydroxide solution, and treated with 60-70 ml of 2*N* sodium sulphide reagent[5], followed by a sufficient excess of 12*N* hydrochloric acid and 10-15 g of ammonium acetate (solid). The concentration of the acid in the resulting solution should be adjusted at a little above 6*N*. The mixture was heated to boiling to dissolve lead sulphide and completely precipitate platinum as sulphide. The precipitate of platinic sulphide was allowed to settle, filtered through a weighed, sintered glass crucible (porosity 4), washed 4-5 times with 5-10 ml portions of hot 6*N* hydrochloric acid (reserve the filtrate for the estimation of lead), and then washed thoroughly with water, alcohol and ether, successively, dried in an air-oven at 105°C for an hour and weighed as sulphide[4].

The filtrate was concentrated to about 25 ml, the free acid neutralized with 8*N* sodium hydroxide, and the ice-cold solution treated with 20-25 ml of 2*N* sodium sulphide reagent followed by a large excess of 6*N* acetic acid. The mixture was heated to boiling, the precipitate of lead sulphide filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with alcohol and ether, successively, dried in a vacuum desiccator for half an hour and weighed.

The results are given in Table I.

TABLE I

DETERMINATION OF PLATINUM AND LEAD IN A MIXTURE WITH 2*N* SODIUM SULPHIDE REAGENT

Wt of Pt in the sulphide g	*Wt of Pt actually present* g	*Wt of Pb in PbS* g	*Wt of Pb actually present* g
0.02155	0.02149	0.06053	0.06061
0.02143	0.02149	0.04850	0.04850
0.01719	0.01719	0.07318	0.07326

Separation of gold from lead

Measured portions of the standard solutions of lead acetate[3] and auric chloride[6] were mixed together. The mixture was treated as given in the separation of platinum from lead. The precipitate of auric sulphide was dried at 105°C for an hour and weighed.

In the filtrate, lead was estimated as sulphide.

The results are given in Table II.

TABLE II

DETERMINATION OF GOLD AND LEAD IN A MIXTURE WITH 2N SODIUM SULPHIDE REAGENT

Wt of Au in Au_2S_3 g	*Wt of Au actually present* g	*Wt of Pb in PbS* g	*Wt of Pb actually present* g
0.03159	0.03167	0.06045	0.06061
0.03167	0.03167	0.04841	0.04850
0.02532	0.02540	0.07326	0.07326

Separation of selenium from lead

Measured portions of the standard solutions of lead acetate[3] and potassium selenite[7] were mixed together, the precipitate of lead selenite was dissolved in the minimum quantity of 8N sodium hydroxide solution. The mixture was subsequently treated as given in the separation of platinum from lead. The precipitate of selenium sulphide was washed with hydrochloric acid and then thoroughly with water only, dried at 95°C for an hour and weighed.

In the filtrate lead was estimated as sulphide.

The results are given in Table III.

TABLE III

DETERMINATION OF SELENIUM AND LEAD IN A MIXTURE WITH 2N SODIUM SULPHIDE REAGENT

Wt of Se in SeS_2 g	*Wt of Se actually present* g	*Wt of Pb in Pbs* g	*Wt of Pb actually present* g
0.08185	0.08191	0.07308	0.07326
0.08185	0.08191	0.05853	0.05861
0.06551	0.06552	0.07318	0.07326

Separation of arsenic from lead

Measured volumes of the standard solutions of lead acetate[3] and potassium arsenate[7] (Kahlbaum's) were mixed together and treated with 8N sodium hydroxide solution to dissolve lead arsenate. In one set of experiments the solution was treated with 60-70 ml of 2N sodium sulphide reagent[5] followed by 10-15 g of ammonium acetate (solid) in the cold. The mixture was shaken for a minute to complete the precipitation of lead as sulphide. The precipitate of lead sulphide was filtered through a weighed sintered glass crucible (porosity 4) and weighed after suitable treatment[3]. In another set of experiments the solution containing lead and arsenic was treated as given in the separation of platinum from lead and the arsenic estimated as As_2S_5. Lead can also be estimated as sulphide in the filtrate from the arsenic sulphide but this takes more time than in the procedure given above.

The results are given in Table IV.

TABLE IV

DETERMINATION OF ARSENIC AND LEAD IN A MIXTURE WITH 2N SODIUM SULPHIDE REAGENT

Wt of Pb in Pbs g	*Wt of Pb actually present* g	*Wt of As in As_2S_5* g	*Wt of As actually present* g
0.06053	0.06061	0.03163	0.03169
0.04841	0.04850	0.03163	0.03169
0.06053	0.06061	0.02531	0.02535

Separation of rhenium from lead

Measured volumes of the standard solutions of lead acetate[3] and potassium perrhenate[8] were mixed together, lead was estimated as sulphide and rhenium as heptasulphide by adopting the procedure given in the separation of arsenic from lead. The precipitate of rhenium heptasulphide was dried in a vacuum desiccator for half an hour and weighed as Re_2S_7. Lead can also be estimated as sulphide in the filtrate from rhenium heptasulphide but this takes more time.

The results are given in Table V.

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TABLE V

DETERMINATION OF RHENIUM AND LEAD IN A MIXTURE WITH $2N$ SODIUM SULPHIDE REAGENT

Wt of Pb in PbS g	*Wt of Pb actually present* g	*Wt of Re in Re_2S_7* g	*Wt of Re actually present* g
0.06053	0.06061	0.03089	0.03095
0.06061	0.06061	0.02471	0.02477
0.04841	0.04850	0.03089	0.03095

Separation of molybdenum from lead

Measured volumes of the standard solutions of lead acetate[3] and ammonium molybdate[9] (Kahlbaum's, prepared with ammonium hydroxide) were mixed together and the procedure given in the separation of arsenic from lead was followed. Lead was estimated as sulphide. The precipitate of molybdenum trisulphide was dried in a vacuum desiccator for an hour and weighed.

Lead can also be estimated as sulphide in the filtrate from molybdenum trisulphide but this takes more time.

The results are given in Table VI.

TABLE VI

DETERMINATION OF MOLYBDENUM AND LEAD IN A MIXTURE WITH $2N$ SODIUM SULPHIDE REAGENT

Wt of Pb in PbS g	*Wt of Pb actually present* g	*Wt of Mo in sulphide* g	*Wt of Mo actually present* g
0.06053	0.06061	0.05014	0.05023
0.06053	0.06061	0.04018	0.04019
0.04850	0.04850	0.05019	0.05023

Note on the separation of tellurium, antimony and tin from lead

When solutions of potassium tellurite and lead acetate are mixed together, lead tellurite gets precipitated. This is insoluble in sodium hydroxide but soluble in hydrochloric acid. The precipitate of lead sulphide, obtained by treating the acid solution with $2N$ sodium sulphide reagent followed by ammonium acetate (solid), is found to be contaminated with sulphur and gives high results. The same difficulty is experienced in separating lead from a tellurate or antimonate. Also, it is not possible to estimate lead in the presence of tin as the precipitate of lead sulphide obtained by adding excess of sodium sulphide reagent has a marked tendency to peptize.

SUMMARY

It has been shown that it is possible to determine platinum, gold, selenium, arsenic, rhenium or molybdenum in the presence of lead with $2N$ sodium sulphide reagent but not tellurium, antimony and tin.

RÉSUMÉ

On démontre qu'il est possible de doser le platine, l'or, le sélénium, l'arsenic, le rhénium ou le molybdène en présence du plomb, avec du sulfure de sodium $2N$, mais non pas le tellure, l'antimoine ou l'étain.

ZUSAMMENFASSUNG

Es wurde gezeigt, dass Platin, Gold, Selen, Arsen, Rhenium und Molybdän, nicht aber Tellur, Antimon und Zinn in Gegenwart von Blei mit $2N$ Natriumsulfid bestimmt werden können.

REFERENCES

[1] G. B. S. Salaria, *Anal. Chim. Acta*, 16 (1957) 3.
[2] G. B. S. Salaria, *ibid.*, 17 (1957) 390.
[3] I. K. Taimni and G. B. S. Salaria, *ibid.*, 11 (1954) 54.
[4] G. B. S. Salaria, *ibid.*, 17 (1957) 395.
[5] I. K. Taimni and G. B. S. Salaria, *ibid.*, 13 (1955) 28.
[6] I. K. Taimni and R. P. Agarwal, *ibid.*, 10 (1954) 312.
[7] I. K. Taimni and R. P. Agarwal, *ibid.*, 9 (1953) 121.
[8] I. K. Taimni and G. B. S. Salaria, *ibid.*, 12 (1955) 519.
[9] I. K. Taimni and R. P. Agarwal, *ibid.*, 9 (1953) 203.

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THE APPLICATION OF THIOSALTS IN ANALYSIS

II. ESTIMATIONS BASED ON DECOMPOSITION OF THIOSALTS PART E. ESTIMATION OF ANTIMONY IN ANTIMONATE

by

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In an earlier publication[1] of this series, it was shown that trivalent antimony can be estimated as sulphide by decomposing the thiosalt with dilute hydrochloric acid.

No satisfactory method is available for the estimation of pentavalent antimony. The methods[2,3,4] known so far involve its reduction to the trivalent state before estimating it as trisulphide or tetroxide. Investigations carried out in this laboratory have shown that if the thiosalt formed by the addition of a large excess of the alkali sulphide reagent to a solution containing pentavalent antimony is decomposed with 2*N* hydrochloric acid, antimony is completely precipitated as antimony pentasulphide and after suitable treatment can be weighed directly for the estimation of the metal.

EXPERIMENTAL

Estimation of antimony as pentasulphide

A solution of potassium hydrogen antimonate (E. Merck Guaranteed Reagent) was prepared and the exact quantity of antimony in it was determined by first reducing it to the trivalent state with mercury[5] in the presence of hydrochloric acid and then titrating with potassium bromate[6].

Measured volumes of the standard potassium hydrogen antimonate solution were treated with 40-50 ml of 2*N* sodium sulphide reagent[7] and the thiosalt formed was decomposed with a sufficient excess of 2*N* hydrochloric acid. The concentration of the acid in the resulting mixture should be about 1*N*. The mixture was heated to boiling and then allowed to cool to room temperature. The precipitate of antimony pentasulphide was filtered through a weighed, sintered glass crucible (porosity 4), thoroughly washed successively with water, alcohol and ether, dried in a vacuum desiccator for half an hour and weighed as Sb_2S_5. Alternatively, the precipitate, after being washed with distilled water and alcohol may be dried in an air-oven at 100-105°C for an hour and weighed.

The results are given in Table I.

TABLE I

DETERMINATION OF PENTAVALENT ANTIMONY WITH 2*N* SODIUM SULPHIDE REAGENT

Wt of Sb in Sb_2S_5 *g*	*Wt of Sb actually present g*
0.04523	0.04524
0.04516	0.04524
0.03612	0.03619

Note on the estimation of platinum

In the case of platinum, it was shown that platinum sulphide obtained by decomposing its thiosalt with hydrochloric acid alone could not be weighed directly and had to be ignited to metal[1].

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It was also shown subsequently that if the thiosalt is decomposed with acetic acid and ammonium acetate, the precipitated sulphide[8] can be weighed directly. Further investigations have shown that if the thiosalt formed by adding excess of the alkali sulphide reagent is decomposed with concentrated hydrochloric acid and ammonium acetate (solid), the precipitated sulphide can be weighed directly for the estimation of the metal after drying in a vacuum desiccator or at 105°C for an hour. But in this case the ratio

$$\frac{\text{weight of the metal}}{\text{weight of the precipitated sulphide}} \text{ is } 0.6229.$$

corresponding to $PtS_2 \cdot 3HO$. $_2$

The results are given in Table II.

TABLE II

DETERMINATION OF PLATINUM WITH $2N$ SODIUM SULPHIDE REAGENT

Wt of Pt in the sulphide g	*Wt of Pt actually present* g
0.02149	0.02149
0.02143	0.02149
0.01713	0.01719

Note on the estimation of lead

In an earlier publication[9] it was pointed out that $2N$ sodium sulphide reagent alone cannot be used for the estimation of lead as sulphide. Further investigation has shown that if the solution containing lead is treated with excess of sodium hydroxide solution and sodium sulphide reagent followed by 10-15 g of ammonium acetate (solid), the precipitated lead sulphide can be weighed directly after the usual treatment. Ammonium sulphide gives equally good results. If sodium sulphide is added to an acid solution containing lead, high results are obtained.

The results are given in Table III.

TABLE III

DETERMINATION OF LEAD WITH $2N$ SODIUM SULPHIDE REAGENT AND AMMONIUM ACETATE

Wt of Pb in PbS g	*Wt of Pb actually present* g
0.06053	0.06061
0.04841	0.04850
0.02425	0.02425

SUMMARY

1. It has been shown that pentavalent antimony can be precipitated quantitatively by decomposing its thiosalt with a large excess of $2N$ hydrochloric acid and weighed as Sb_2S_5.

2. In the case of platinum, $12N$ hydrochloric acid can be substituted for acetic acid in the decomposition of the thiosalt.

3. Lead can be quantitatively estimated as sulphide by sodium sulphide if ammonium acetate is also added.

RÉSUMÉ

1. On démontre que l'antimoine pentavalent peut être précipité quantitativement en décomposant son thio-sel avec un grand excès d'acide chlorhydrique $2N$ et pesé comme Sb_2S_5.

2. Dans le cas du platine, l'acide chlorhydrique $12N$ peut être substitué à acétique dans la décomposition du thio-sel.

3. Le plomb peut également être dosé comme sulfure par le sulfure de sodium à condition d'ajouter de l'acétate de sodium.

ZUSAMMENFASSUNG

1. Es wurde gezeigt, dass fünfwertiges Antimon quantitativ gefällt werden kann indem man sein Thiosalz mit einem grossen Überschuss an 2*N* Salzsäure zersetzt und als Sb_2S_5 wägt.
2. Im Falle des Platins kann 12*N* Salzsäure die Essigsäure bei der Zersetzung des Thiosalzes ersetzen.
3. Blei kann quantitativ mit Natriumsulfid als Sulfid bestimmt werden, wenn auch Ammoniumacetat zugefügt wird.

REFERENCES

[1] I. K. TAIMNI AND R. P. AGARWAL, *Anal. Chim. Acta*, 10 (1954) 312.

[2] F. HENZ, *Z. anorg. Chem.*, 37 (1903) 18.

[3] G. VORTMANN AND A. METZL, *Z. anal. Chem.*, 44 (1905) 532.

[4] W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. E. HOFFMAN, *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, Inc., New York, 1953, p. 282.

[5] S. GYÖRY, *Z. anal. Chem.*, 32 (1893) 415.

[6] H. W. ROWELL, *J. Soc. Chem. Ind. (London)*, 25 (1907) 1181.

[7] I. K. TAIMNI AND G. B. S. SALARIA, *Anal. Chim. Acta*, 13 (1955) 28.

[8] I. K. TAIMNI AND G. B. S. SALARIA, *ibid.*, 11 (1954) 329.

[9] I. K. TAIMNI AND G. B. S. SALARIA, *ibid.*, 11 (1954) 54.

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A SIMPLIFIED AND EXTENDED SCHEME OF ANALYSIS FOR THE COMMON CATIONS, BASED ON PAPER CHROMATOGRAPHY

by

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The use of paper chromatography for the projection of a scheme of analysis for the common cations, based solely on paper chromatography, has already been established[1]. However, the need for a simplified and extremely accurate technique has never been abandoned. The first scheme of analysis[1] which came to be known as the chromatogram-comparison method[2] was originally based on the use of three different solvent mixtures, namely, the butanol-benzoylacetone, the collidine, and the dioxan-antipyrine solvent mixtures. The location, identification, and tentative confirmation of the precense of cations was made by six general sprays, in the combination with comparing the R_F values of cations in different solvent mixtures, as indicated by respective chromatograms.

In the present work the chromatogram-comparison method has been extended to include—other than the common cations—the elements Li, Be, Ti, Ce, V, Mo, Th and U. The scheme has also been simplified so that only six strip-chromatograms, two on each solvent mixture, would suffice to carry out the location, identification and confirmation of the presence of cations. Confirmatory tests by the use of specific spot reagent sprays has been introduced to make the method extremely accurate.

EXPERIMENTAL AND RESULTS

Preliminary investigation of the powder should be carried out in both the dry and wet way[3] as it is necessary to test for the presence of phosphate, borate, arsenite, arsenate, tartrate, oxalate, formate, acetate, citrate and ammonium radicals.

Dissolution of the powder

In absence of the above-mentioned radicals, the solution is prepared by boiling about 0.2 g portion of the powder with 2 ml of 2*N* nitric acid. Any dichromate, chromate, or permanganate anions present are converted into their respective cations by adding a few drops of hydrogen peroxide until the colour of the anion disappears. The solution is centrifuged after cooling to remove any precipitate, and the clear supernatant solution is diluted with distilled water till the concentration of acid in the solution is approximately 0.1*N*. This solution is used for the analysis. If any insoluble salts are present, they are removed by centrifuging and dealt with separately. They can be brought into solution by fusion with sodium carbonate, and chromatographed alone.

Removal of interfering radicals

The presence of certain radicals interferes with the movement of some cations. It is advisable to remove such radicals before preparing the solution for chromatographic analysis.

(1) *Removal of tartrate, oxalate, formate, acetate, citrate anions and the ammonium cation.* The original solution of the powder is tested first for the presence of sodium by the zinc uranyl acetate method[2]. Then the original powder is mixed with about half of its weight of anhydrous sodium carbonate and the mixture heated to redness in a crucible. The anions mentioned will be decomposed and the ammonium cation is removed as ammonia. The resulting solid is cooled and dissolved in nitric acid as described above for the preparation of the solution for analysis.

(2) *Removal of phosphate, borate, arsenite and arsenate anions.* These anions can be removed by the use of ion-exchange resins. The solution for the ion-exchange column is prepared in one of two ways:

(a) If the original powder contains one or more of the ions mentioned in No. (1) above; these ions should be removed first — as indicated — and the residue is used to prepare the solution as given below.

(b) If the ions mentioned in No. (1) are absent from the original powder; this is used directly to prepare the solution. 0.2 g portion of the solid from (a), or from the original powder, is boiled with 2 ml of 2*N* hydrochloric acid. Any (di)chromate or permanganate anions present are converted into their respective cations by adding a few drops of hydrogen peroxide until the colour of the anion disappears. The solution is centrifuged to remove any precipitate which may consist of Ag, Hg^+, Pb or salts such as barium sulphate. These can be brought into solution by the method of fusion with sodium carbonate, and chromatographed alone. The clear supernatant solution is diluted to double its volume by distilled water, then allowed to pass through a small column of Zeocarb 215, already prepared, soaked with *N* hydrochloric acid and washed with distilled water[2]. The cations are absorbed on the resin while the anions are removed in the eluate. After the complete removal of the anions, 5*N* hydrochloric acid solution is passed through the column to displace the cations, which will appear in the eluate. The eluate is evaporated to a very small amount, then diluted with distilled water to adjust the acidity of the remaining solution of cations until it corresponds to approximately 0.1*N*. The resulting solution is used for the analysis. It is important in all the above-mentioned reactions to use A.R. reagents, since this type of analysis is very sensitive and impurities in the reagents may cause confusion on chromatograms.

Preparation of the chromatograms

The apparatus is similar to that, already in general use for paper chromatography[2] and consists of a glass trough supported in a glass tank 50 × 25 × 15 cm tightly covered with a glass plate. The alcoholic layer of the solvent is put in the trough and at the bottom of the tank is placed a Petri dish containing the aqueous layer of the solvent, *e.g.* in benzoylacetone and collidine; or some of the solvent if it constitutes only one layer, *e.g.* in dioxan. The tanks containing the different solvent mixtures are placed in an insulated cupboard, kept at room temperature.

Filter paper sheets are cut into strips 10 cm wide and 40 cm long and the trough height is adjusted to permit hanging paper strips from both sides of the trough with their top edges dipping into the solvent.

TABLE I

APPEARANCE OF CATIONS UNDER ULTRAVIOLET LIGHT AFTER SPRAYING WITH THE KOJIC ACID-OXINE MIXTURE

Bright spots			*Dark spots*		
+ + +	+ +	+	− − −	− −	−
	Ag (yellow)	Th (yellowish-green)	Hg^{2+}, Bi (dark brown)	Pb (dark grey)	
Al (whitish-yellow)	Sn^{4+} (blue)		Ce (dark violet)		Cr, K, Na, Li (violet)
Cd, Zn (bright yellow)	Sn^{2+} (dirty yellow)		Mo (brown)		
Mg, Be (white)	Ca, Sr, Ba (whitish blue)		Hg^{+}, Cu, Fe, Mn, Co, V, Ni, U, Ti (black)		

N.B. As and Sb are not detected.

TABLE II

APPEARANCE OF CATIONS IN DAYLIGHT AFTER SPRAYING WITH THE KOJIC ACID-OXINE MIXTURE

Colour	*Cation*	*Colour*	*Cation*	*Colour*	*Cation*
Light brown	Ag, Ce	green	Cu	black	Fe
Yellow-brown	Mn, Co, V	yellow	Ti	reddish-brown	U
Bright yellow	Hg^{2+}	pale yellow	Pb, Bi, Cd, Zn, Mo, Th, Al, Sn^{2+}	colourless	Ca, Sr, Ba, Na, K, Mg, Li, Be, As, Sb, Sn^{4+}
Yellow-green	Cr, Ni, Hg^{+}				

Three separate tanks are required. One of the three general solvent mixtures is placed in each tank. They are prepared as follows:

(1) The butanol-benzoylacetone solvent: 50 ml N butanol + 50 ml 0.1N nitric acid and 0.5 g benzoylacetone.

(2) The collidine-nitric acid solvent: 50 ml collidine + 50 ml 0.4N nitric acid.

(3) The dioxan-antipyrine solvent: 100 ml dioxan + 1 ml conc. nitric acid + 1 g phenazone + 2.5 ml water.

Only 6 drops of the solution of the powder are needed for the complete analysis. Two drops (1 cm diameter) of the solution are placed at distances of 5 cm along the starting line of a strip of filter paper (10 cm wide and 40 cm long). When analysing more than one unknown solution, more strips must be used on both sides of the same trough. Paper strips — carrying only two drops each — are prepared in triplicates, one for each solvent mixture, and strips are placed in the respective tanks. With the different rates of flow of the solvent mixtures, different times will be needed to allow the solvent front in all solvents to flow a distance of at least 30 cm from the starting line. On the collidine solvent this takes about 44 hours; with the benzoylacetone it takes about 22 hours, while on the dioxan it would take about 10 hours only.

Analysis of the chromatograms

The strips — carrying two drops each — are removed from the tanks and dried in a stream of hot air. Each strip is cut longitudinally into two individual strips carrying one drop each of the unknown solution. The six individual strips — two from each tank — are divided into two groups:

(a) Three locating strips; one from each tank.

(b) Three confirmatory strips; one also from each tank.

The whole procedure of analysis is carried out on these six strips as follows:

(A) The three locating strips are first sprayed with a solution containing 1 g kojic acid and 5 g 8-hydroxyquinoline in 1 l of 60% alcohol. The strips are dried, then viewed under the ultraviolet light while treating them with ammonia vapour. The positions of certain cations are revealed as dark or fluorescent spots with different characteristic colours according to Table I. The centre of gravity of each revealed spot is marked with a pencil. The strips are removed from the ultraviolet light to be viewed in the daylight. This will not reveral the position of more cations but it will help in the identification of some of the located spots according to Table II.

The colours observed under the ultraviolet light and in daylight are due to the formation of coloured metallic oxinates. The three locating strips are again sprayed with ammoniacal hydrogen sulphide water and dried. This will lead to the formation of some coloured sulphides as indicated in Table III.

TABLE III

APPEARANCE OF CATIONS IN DAYLIGHT AFTER SPRAYING WITH KOJIC ACID-OXINE MIXTURE, THEN WITH AMMONIACAL HYDROGEN SULPHIDE WATER

Colour	*Cations*
Yellow	Cd, As, Th, Ti, Sn^{2+}
Light brown	Mn, Ce
Brown	Ag, Cu, Hg^{2+}, V
Chocolate-brown	Pb
Orange	Sb, U
Pale green	Cr
Black	Hg^{+}, Bi, Fe, Co, Ni

The centres of gravity of the newly revealed spots are marked with a pencil. The R_F values of all the revealed spots on the three locating strips are calculated and compared with the R_F values given in Table IV (location table). The R_F values, as well as the colours of oxinates under the ultraviolet light, in daylight and the colours of sulphides will give a definite idea regarding the identity of some cations. In other spots, it would give a clear idea whether the spot revealed may be one of two or more possibilities. All possibilities are noted and then, consulting Table V (confirmation table), one should be able to decide the limited number of cations, the presence of which could be confirmed on each strip of the confirmatory strips. After making this decision with reference to Table V, one should proceed with the confirmatory sprays.

(B) Each locating strip is placed beside its twinstrip from the confirmatory group. Pencil dots which were placed on the locating strips to mark the centre of gravity of the spots are duplicated

on the confirmatory strips only in those places where it bas heen decided to apply confirmatory sprays (according to *(A)*). The confirmatory strips are now ready for different types of sprays. This is carried out by using a large thin sheet of aluminium (30 × 15 cm) in which is cut a small window 6 cm long and 5 mm high. The confirmatory sprays are applied through this window. The confirmatory strips are suspended from a supported glass rod using plastic clothes-pegs to fasten the upper edges of the strips to the rod. The lower edges of the strips are clamped by heavy "bulldog" clips to keep the paper stretched without holding it by the hand.

The aluminium sheet with the window is then held in the left hand, one cm in front of the paper-strip without touching it and the specific sprays applied by the right hand. When applying any specific spray the window is adjusted in front of the paper-strip, making certain that the required centre of gravity of spot (marked by a pencil dot) is in the centre of the window. The specific materials are applied by fine sprays across the window. The aluminium sheet is always washed and dried after each experiment and kept ready for further work. The specific spray will — in all experiments — stain the middle part of the window (the spot) with the expected colour, which may be distinguished from the colour of the background observed on the lateral sides of the spot (Fig. 1).

The following list gives the specific sprays which could be used to confirm the presence of cations. Only one corfirmatory spray is given for each cation, and this was found to be completely satisfactory for all cations under investigation.

LIST OF CONFIRMATORY SPRAYS

Silver: R_F value 0.78 on the collidine strip. *p*-Dimethylaminobenzalrhodanine: 0.1 g in 100 ml of acetone[4]. The strip is sprayed first with 2*N* nitric acid, then dried and sprayed with the reagent; a red colour indicates silver.

Mercury: R_F value 0.42 on the dioxan strip. Diphenylcarbazone: 1 g in 100 ml of methylated spirit[4]. A deep blue colour is obtained.

Lead: R_F value 0.15 on the dioxan strip. Gallocyanine: 1 g in 100 ml of distilled water[3]. The strip is first sprayed with 2*N* ammonia solution then dried, and sprayed with the reagent. A red-violet colour indicates lead.

Bismuth: R_F value 0.63 on the dioxan strip. Cinchonine-potassium iodide: 1 g of cinchonine in 100 ml of hot water containing a little nitric acid. After cooling, 2 g of potassium iodide are added[3]. An orange-red colour indicates bismuth.

Copper: R_F value 0.24 on the dioxan strip. Sodium diethyldithiocarbamate: 0.2 g in 100 ml of methylated spirit. A yellowish-brown colour appears.

Cadmium: R_F value 0.18 on the dioxan strip. 8-Hydroxyquinoline: 0.5 g in 100 ml of methylated spirit. A bright golden-yellow spot appears under the ultraviolet light.

Arsenic: R_F value 0.43 on the benzoylacetone strip. Diphenylthiocarbazone: 0.05 g in 100 ml of chloroform (freshly prepared). A rose-pink colour appears immediately.

Antimony: R_F value 0.00 on the benzoylacetone strip. Ammonium sulphide: equal volumes of yellow bench solution and distilled water[2]. An orange colour indicates antimony.

Tin: R_F value 0.58 on the benzoylacetone strip. Dithiol: 0.2 g toluene-3,4-dithiol are dissolved in 100 ml of 1% sodium hydroxide solution and about 0.3 g of thioglycollic acid are added (freshly prepared)[4]. A red colour indicates tin.

Aluminium: R_F value 0.00 on the collidine strip. Aluminon: 0.1 g in 100 ml of 1% ammonium acetate in distilled water[2]. The strip is sprayed first with normal nitric acid, dried, and then sprayed with the reagent. A bright red colour is obtained on exposing the strip to ammonia vapour.

Chromium: R_F value 0.01 on the dioxan strip. Diphenylcarbazide: 1 g in 90 ml of methylated spirit, then 10 ml of glacial acetic acid are added. A deep violet colour is obtained on gentle warming of the strip.

Iron: R_F value 0.95 on the benzoylacetone strip. Potassium ferrocyanide: 5 g in 100 ml of distilled water[2]. The strip is sprayed first with 2*N* nitric acid, dried and then sprayed with the reagent. A prussian-blue colour is obtained.

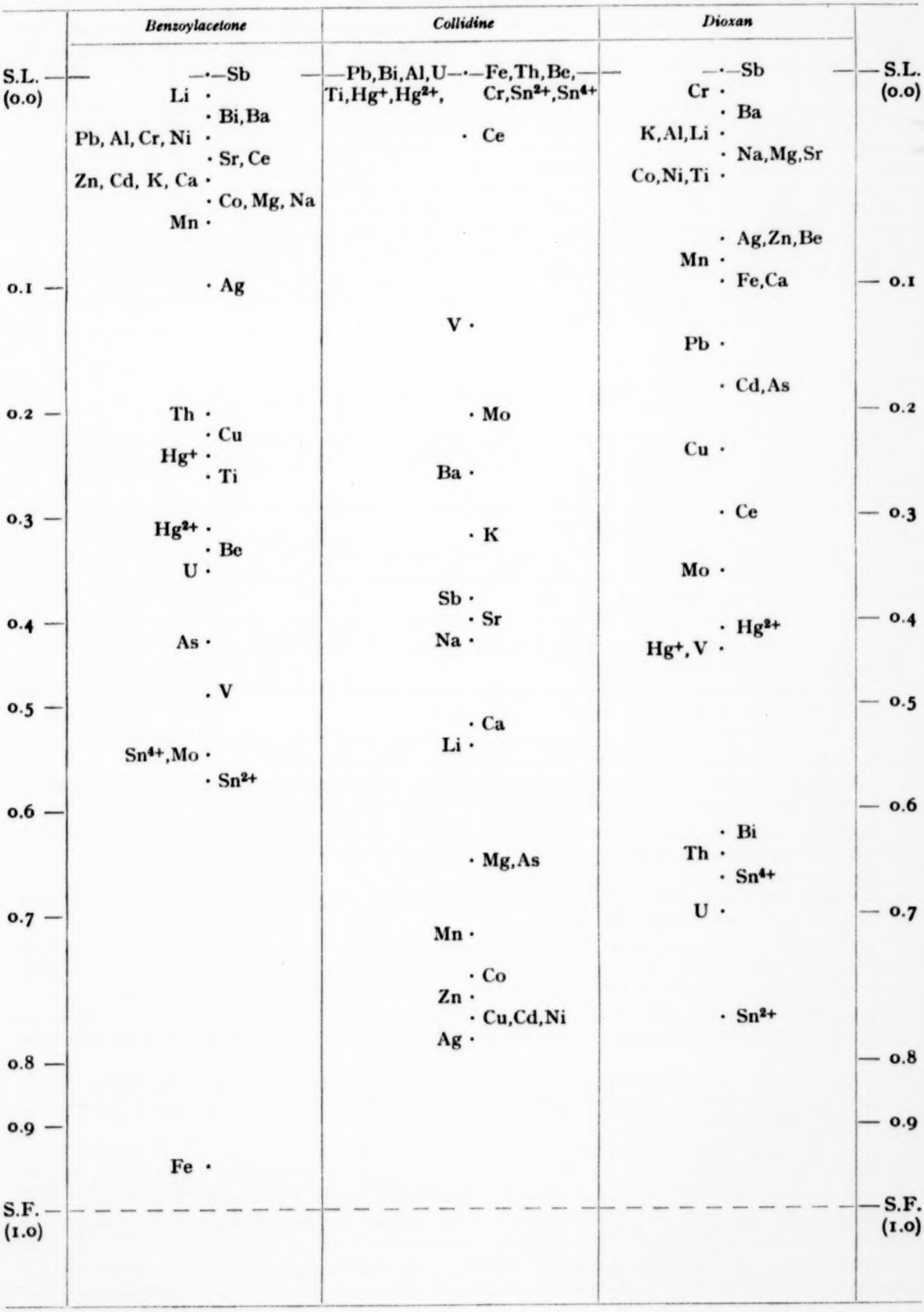
Zinc: R_F value 0.08 on the dioxan strip. 8-Hydroxyquinaldine: 0.5 g in 100 ml of methylated spirit. A moderately bright yellow fluorescent spot is obtained on exposure to ammonia vapour. If sprayed with glacial acetic acid it changes to an intense bright whitish-yellow fluorescent spot.

Manganese: R_F value 0.71 on the collidine strip. Sodium diethyldithiocarbamate: prepared as in copper. A chocolate-brown colour indicates manganese.

Cobalt: R_F value 0.06 on the benzoylacetone strip. 1-Nitroso-2-naphthol: 2 g in 100 ml of methylated spirit[4]. A deep brownish-red colour indicates cobalt.

TABLE IV

LOCATION TABLE



Nickel: R_F value 0.76 on the collidine strip. Dimethylglyoxime: 1 g in 100 ml of methylated spirit[2]. The strip is sprayed with the reagent, then exposed to ammonia vapour; a bright red color is formed.

Calcium: R_F value 0.52 on the collidine strip. Pyrogallol: 1 g in 100 ml of 10% ammonium hydroxide solution (freshly prepared). A distinct brown spot is formed, comparable with the dull yellow background.

Strontium: R_F value 0.40 on the collidine strip. Pyrogallol: prepared as in calcium. A distinct brown spot indicates strontium.

Barium: R_F value 0.26 on the collidine strip. Pyrogallol: prepared as in calcium. A distinct brown spot indicates barium.

Magnesium: R_F value 0.65 on the collidine strip. Titan yellow: 0.1 g in 100 ml of distilled water[4]. The strip is sprayed first with $2N$ sodium hydroxide solution, then dried, and sprayed with the reagent. A bright red colour indicates magnesium.

Potassium: R_F value 0.32 on the collidine strip. Dipicrylamine: prepared by dissolving 0.2 g in 20 ml of boiling $2N$ sodium carbonate solution and filtering the cooled liquid[3]. The strip is sprayed with the reagent, dried and then sprayed gently with $2N$ hydrochloric acid. An orange-red spot indicates potassium.

Sodium: R_F value 0.42 on the collidine strip. Zinc uranyl acetate: saturated solution in $2N$ acetic acid and then filtered[2]. A blue fluorescent spot is formed in absence of ammonia vapour.

Lithium: R_F value 0.54 on the collidine strip. Zinc uranyl acetate: prepared as in sodium. A blue fluorescent spot is formed in absence of ammonia vapour.

Beryllium: R_F value 0.33 on the benzoylacetone strip. p-Nitrobenzeneazo-orcinol: 0.1 g in 100 ml of acetone[4]. The strip is sprayed first with $2N$ sodium hydroxide solution, then dried, and sprayed with the reagent. A deep orange-red colour is obtained and fades gradually.

Cerium: R_F value 0.30 on the dioxan strip. Benzidine: 0.05 g in 100 ml of 10% acetic acid[2]. The strip is sprayed first with concentrated ammonium hydroxide solution, then dried and sprayed with the reagent. A bright blue colour indicates cerium.

Titanium: R_F value 0.26 on the benzoylacetone strip. Chromotropic acid: 5 g in 100 ml of distilled water[2]. The strip is sprayed first with the reagent, then dried and sprayed with normal sulphuric acid. A reddish-brown colour appears on gentle warming of the strip.

Vanadium: R_F value 0.13 on the collidine strip. Tannic acid: 10 g in 100 ml of distilled water[2]. A dark grey colour indicates vanadium.

Molybdenum: R_F value 0.20 on the collidine strip. Potassium thiocyanate-acetone: equal volumes of saturated aqueous thiocyanate and acetone[2]. The strip is sprayed first with the reagent, dried and then sprayed with bench solution of stannous chloride. A blood-red colour appears.

Thorium: R_F value 0.20 on the benzoylacetone strip. Diphenylcarbazone: prepared as in mercury. The strip is sprayed first with $2N$ nitric acid, then dried and sprayed with the reagent. A deep violet colour appears on gentle warming of the strip.

Uranium: R_F value 0.70 on the dioxan strip. Potassium ferrocyanide: prepared as in iron. A deep brown colour indicates uranium.

The above procedure was applied to the analysis of a large number of synthetic mixtures each consisting of 6 to 8 cations or more. Very accurate results were obtained. As an example, the analysis of a mixture containing 7 cations is photographed in Fig. 1. In the figure the three confirmatory strips clearly show the presence of the seven cations: Co, Th, Fe, Mn, Ag, Cu and U; sprayed as follows:

Strip I (benzoylacetone strip):
  Co: 1-Nitroso-2-naphthol: a deep brownish-red spot.
  Th: Diphenylcarbazone: a deep violet spot.
  Fe: Potassium ferrocyanide: a prussian-blue spot.

Strip II (collidine strip):
  Mn: Sodium diethyldithiocarbamate: a chocolate-brown spot.
  Ag: p-Dimethylaminobenzalrhodanine: a red spot.

Strip III (dioxan strip):
  Cu: Sodium diethyldithiocarbamate: a yellowish-brown spot.
  U: Potassium ferrocyanide: a deep brown spot.

The procedure was further simplified through the use of ascending chromatography — instead of the descending technique — and was applied successfully in analytical classes by undergraduate students.

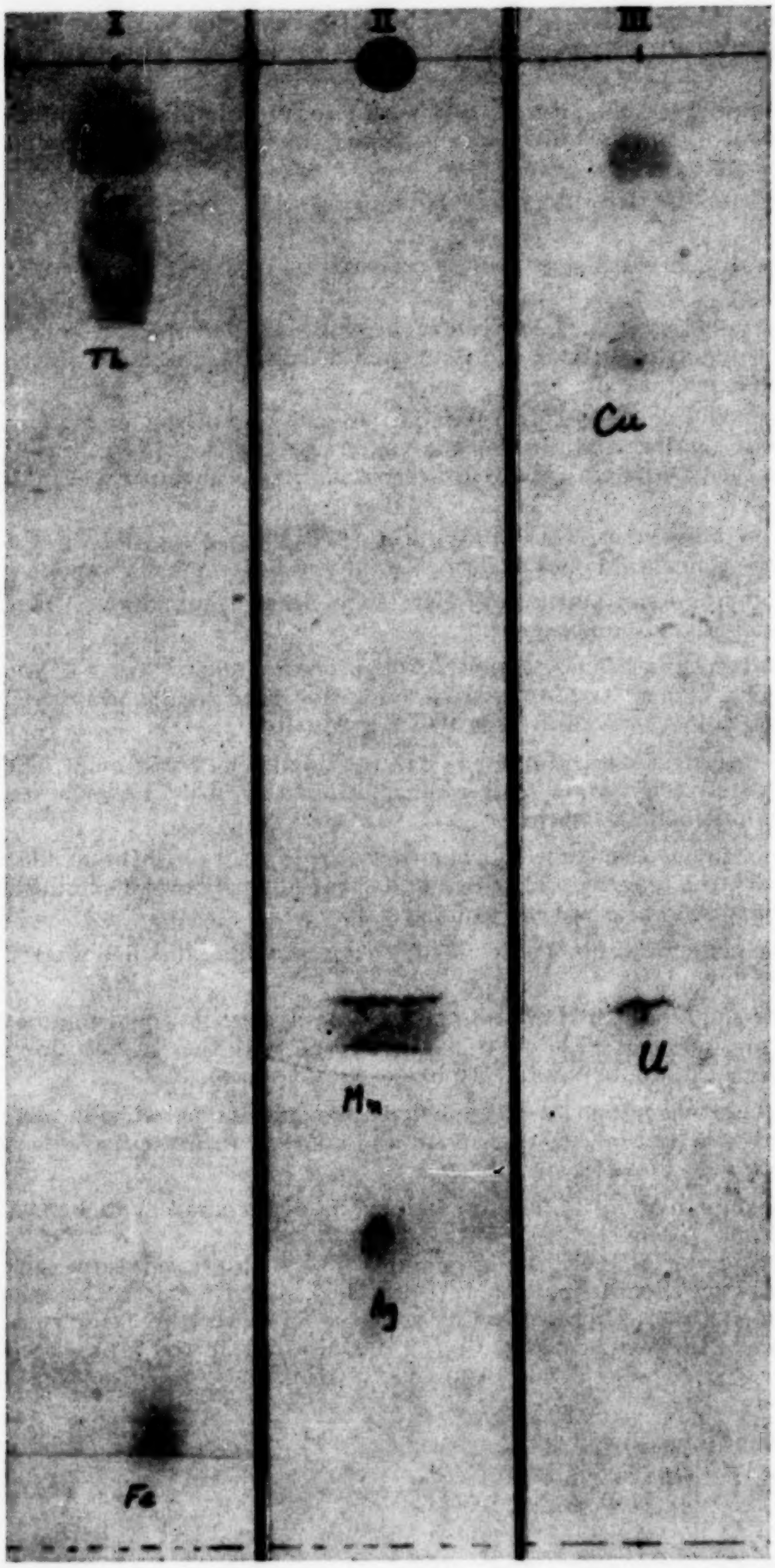

I
II
III
Th
Cu
Mn
U
Ag
Fe

Fig. 1

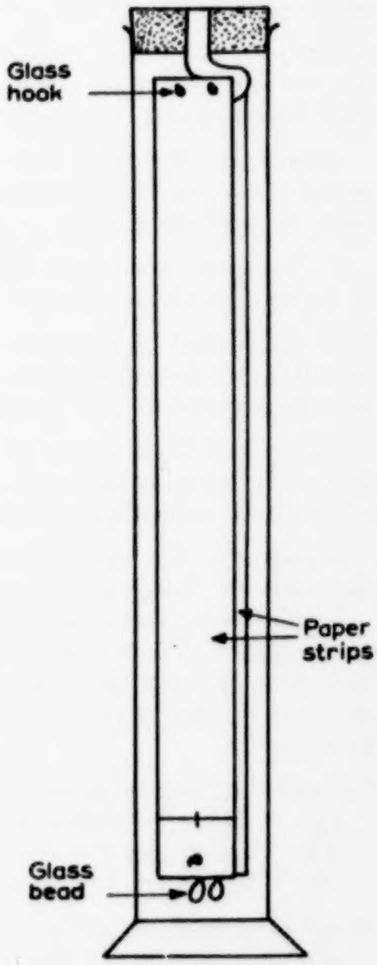

Glass hook
Paper strips
Glass bead

Fig. 2

The apparatus consists of three, one-litre, graduated cylinders, each provided with a tight rubber stopper, through which passes a thick glass rod bent twice at the lower end to form a horizontal part, and carrying two spikes at each side. On each side is hung one paper strip, 4 cm wide (Fig. 2). The solvent mixture is placed at the bottom of the cylinder to a depth of 4 cm. The lower end of the paper strips should be dipping into the solvent. The paper strips are kept taut by means of small glass beads hung on their lower ends. One drop (1 cm diameter) of the solution to be analysed is placed in the middle of a starting line pencilled 5 cm from the lower edge of each paper strip. For the complete analysis of one unknown solution six paper strips are prepared and placed in duplicates in the three graduated cylinders, each containing one of the three general solvent mixtures. When the solvent front for each solvent mixture is at 30 cm or more from the starting line, the strips are removed, dried, and sprayed as given in the general procedure of analysis. Of course, each solvent requires a different length of time to cover the required distance.

DISCUSSION

Although the technique described in this scheme of analysis is fairly simple, there are still certain points to consider in order to obtain the best results. These points are discussed in the following.

(1) The use of approximately 0.1N-acid in the original solution for analysis is of great importance since the R_F values of certain cations (*e.g.* Fe) will be lower in a highly acid medium. If the original spot contains about 0.1N acid the iron spot moves on the benzoylacetone strip with an R_F value 0.95, whereas, if the acid content of the original spot is about 2N, the iron spot moves with an R_F value about 0.65. This is also true for some other cations in other solvent mixtures and it might cause serious interference specially in the application of specific sprays.

(2) It must be emphasized that the specific sprays given in the above list have been selected to be applied in the appropriate positions shown in Table V without the slightest interference from the solvent mixture used for running the paper-strip or from other cations that might be moving to the same position (*i.e.* with the same R_F value). For example, the presence of uranium can be confirmed by spraying with potassium ferrocyanide at an R_F value 0.70 on the dioxan strip without the slightest interference from Sn^{+2} or Sn^{+4} which may be present, while, if the same spray is applied for uranium on the benzoylacetone or collidine strips, other cations present might interfere and give other misleading colours with this particular specific spray.

(3) The kojic acid-oxine spray is capable of revealing stationary spots of cations containing as little as 5 μg of K[5]. This value should be doubled for spots after running on sheet-chromatograms.

Specific sprays are much more sensitive for most cations, *e.g.* about 5 μg of Hg, Fe, Mn, Ni, Th and U could easily be detected by respective specific sprays after running on sheet-chromatograms.

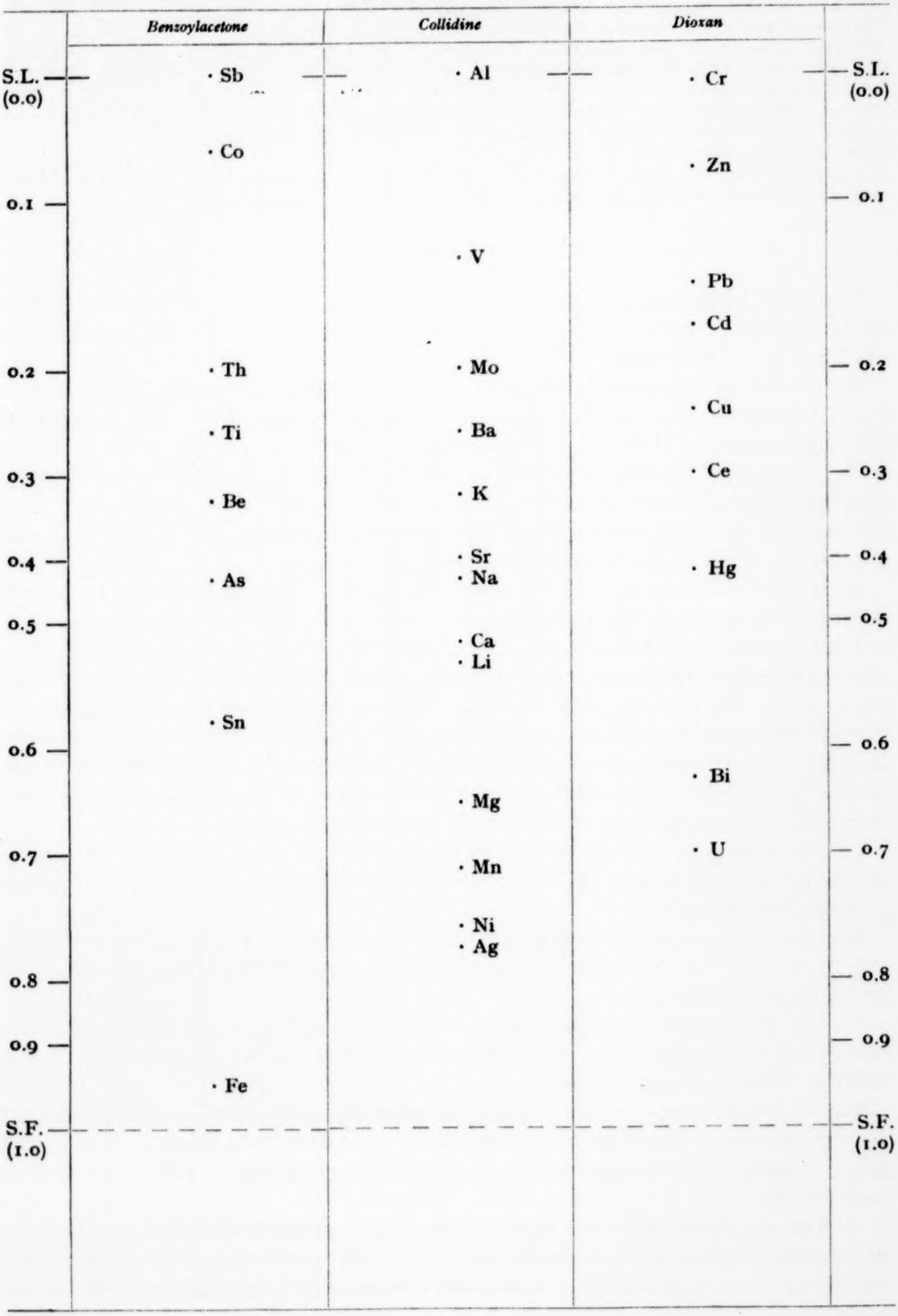
On the other hand, if the original spot contains more than 100 micrograms of a certain cation, trailing of this particular cation is liable to take place and would probably prevent good separations.

The optimum concentration — on the original spot (about 0.01 ml) — for each of the cations, under investigation in this scheme of analysis, was found to lie between 100 and 10 μg. This corresponds to a concentration range from 1 g % — 0.1 g % of each cation.

(4) The aluminium mask has been provided with a narrow window (5 mm high) to prevent interference between specific sprays especially when cations have adjacent R_F values, *e.g.* Pb = 0.15 and Cd = 0.18 on the dioxan strip. It has also been pointed out

TABLE V

CONFIRMATION TABLE



in the procedure that the solvent front must be allowed to run for at least 30 cm from the starting line. The reason for this is to ensure adequate separation of cations like Pb and Cd on the dioxan strip. The separation of these two cations is only one cm if the solvent front moves for 30 cm as indicated. If the window in the aluminium mask is higher than 5 mm, interference of specific sprays will be most probable if Pb and Cd are present in the same mixture. It is always advisable to allow the solvent front to move further than 30 cm if possible. In places where cations are distantly separated, *e.g.* tin and iron on the benzoylacetone strip, it is always possible to move the aluminium mask slightly up and down to cover a larger area without fear of causing any interference.

(5) It is important in this type of analysis to use filter paper sheets specified for chromatography, as ordinary filter paper sheets sometimes contain impurities and may lead to confusing results.

SUMMARY

The chromatogram-comparison method has been extended to include the elements Li, Be, Ce, Ti, V, Mo, Th and U. The technique was simplified through the use of six drops of the original solution, two on each of the general solvent mixtures. The method was also made more accurate through the application of selected specific sprays.

RÉSUMÉ

La méthode chromatographique par comparaison a été étendue aux éléments: Li, Be, Ce, Ti, V, Mo, Th et U. La technique a été simplifiée par l'emploi de 6 gouttes de la solution primitive, dont deux pour chacun des mélanges de solvants. La méthode est également rendue plus précise grâce à l'application de réactifs révélateurs spécifiques.

ZUSAMMENFASSUNG

Die Chromatogramm-Vergleichsmethode wurde auf die Elemente Li, Be, Ce, Ti, V, Mo, Th und U ausgedehnt. Die Arbeitstechnik wurde insofern vereinfacht, als sechs Tropfen der ursprünglichen Lösung verwendet wurden und zwar je zwei Tropfen pro Lösungsmittelgemisch. Ausserdem wurde die Methode durch die Anwendung spezifischer Entwicklungsreagenzien genauer gemacht.

REFERENCES

[1] F. H. POLLARD, J. F. W. McOMIE AND I. I. M. ELBEIH, *J. Chem. Soc.*, (1951) 470.
[2] J. F. W. McOMIE AND F. H. POLLARD, *Chromatographic Methods of Inorganic Analysis*, Academic Press Inc., New York, 1953, 192 pp.
[3] A. I. VOGEL, *Qualitative Chemical Analysis*, 3rd Ed., Longmans, Green & Co. Ltd., London, 1945, 567 pp.
[4] *Organic Reagents For Metals*, Hopkin & Williams Ltd., London, 1946, 176 pp.
[5] F. H. POLLARD, J. F. W. McOMIE AND I. I. M. ELBEIH, *J. Chem. Soc.*, (1951) 466.

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SALTING-OUT CHROMATOGRAPHY

II. AMINES

by

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Mixtures of amines have been separated in milligram quantities by gas-liquid partition[1] and liquid-liquid partition chromatography on celite[2] and silica gel[3]. Although the quantitative determination of the isolated amine is, in some cases, more difficult in the presence of a basic eluant, salting-out chromatography offers the advantages of a higher resolving power and the use of aqueous solvents.

Salting-out chromatography, a process in which non-electrolytes may be separated by elution through a column of ion-exchange resin with aqueous salt solutions as eluants, has recently been applied by the authors to the separation of alcohol mixtures[4,5].

Amines differ from alcohols in their ability to form ions. In order to eliminate ion exchange and to study only the effects of salting-out, a strongly basic eluant was used so that the amines were present as non-electrolytes. Since anion-exchange resins decompose slowly in alkaline solution, a cation exchanger was used exlusively.

The results are interpreted by use of the equation[6]

$$U^* = CV + V \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where U^* is the volume of eluate collected from the addition of the sample to the peak on the elution graph, C is the distribution ratio of the amine and V is the interstitial volume of the column. For Dowex 50-X4, 200-400 mesh, the value of V was found to be 34% of the bed volume by the method of RIEMAN AND LINDENBAUM[7].

EXPERIMENTAL

Resin

The strong-acid cation-exchange resin, Dowex 50, was converted to the potassium form by washing with 1M tripotassium phosphate and packed as previously reported[5]. Unless specified, the resin used was cross-linked with 4% divinylbenzene.

Apparatus and reagents

Fractions of 6.0 ml were collected with an automatic constant-volume fraction collector[6]. All amines were the best grade obtainable. *n*-Butylamine, aniline and benzylamine were freshly distilled before use. Because commercial tripotassium phosphate contains an indefinite quantity of water, eluants are most conveniently prepared by addition of carbonate-free potassium hydroxide to dipotassium monohydrogen phosphate. The eluant used in this investigation was prepared from the tripotassium salt which contained 0.8% of the monohydrogen salt. This was neutralized by the addition of potassium hydroxide and the solution was analyzed by the titration of phosphate ion between the second and first equivalence points with standard hydrochloric acid.

Analysis of eluate

Four methods were used to determine the concentration of amine in the fractions of eluate.

(1) Mono-, di- and triethanolamines are conveniently and accurately analyzed by mixing them with an equal volume of 0.1*N* potassium dichromate dissolved in concentrated sulfuric acid, followed by measurement of the absorbance of Cr(III)[8] in a 10-cm absorption cell. This method is accurate to ± 0.005 mequiv of reducing agent. Aliphatic amines and pyridine fail to reduce dichromate.

(2) Aliphatic amines which contain a single amino group and tetramethylenediamine may be extracted with chloroform[9]. The fraction of eluate was shaken with 25.0 ml of chloroform. The lower layer was withdrawn and shaken with 4 ml of water to remove a small amount of potassium phosphate. The lower layer was withdrawn again into a 50-ml glass-stoppered cylinder which contained 5 to 10 ml of water and a drop of bromcresol purple indicator solution. This mixture was then titrated with 0.01*N* hydrochloric acid delivered from a 10-ml microburet. Consistant blanks of 0.02 ml were obtained. Quantitative extraction is not essential for the location of elution maxima. The quantity of amine titrated was 0.1 (methylamine) to 0.3 (*n*-amylamine) of the sample with a reproducibility of ± 0.01 ml of 0.01*N* hydrochloric acid.

(3) Aromatic amines have absorption maxima close to 260 mμ, where there is practically no interference from aliphatic amines or potassium phosphate. A sensitivity of roughly 10 times that of the previous methods is obtained. Blanks are high because of organic material being washed from the resin, but no difficulty is encountered in locating the elution maxima. Combination of methods 2 and 3 makes possible the analysis of an eluate fraction which contains both an aliphatic and an aromatic amine.

(4) Ethylenediamine and its polymers cannot be extracted by method 2 in quantities sufficient to determine their elution maxima. These compounds were treated with nitrous acid and the alcohol produced was determined by method 1. To do this, 1 ml of 1*M* sodium nitrite was added to the effluent fraction previously acidified with 5 ml of 50% sulfuric acid in 50-ml beakers. A boiling chip was added and the excess nitrous acid was expelled by boiling the solution for 5 minutes. When cool, the mixture was treated by method 1. The foregoing reactions do not need to be quantitative for locating elution maxima.

RESULTS

A study of the variables which affect salting-out chromatography of amines was carried out in a manner similar to that reported for the alcohols[5]. Since weak-base and weak-acid resins were found to be unsatisfactory for the salting-out chromatography of the alcohols, they were not studied in this work. For the same reason, only resins of 200-400 mesh were used.

Cross-linkage

A mixture of 0.2 mmole each of ethylamine, diethylamine and pyridine was eluted from a column, 9.7 cm × 3.90 sq. cm, of Dowex 50-X8 with 0.88*M* potassium phosphate. The elution graph (Fig. 1A) was compared with similar elutions from columns containing Dowex 50-X4 and Dowex 50-X2. All elutions were run with a flow rate of 0.5 cm per min. Dowex 50-X4 was chosen as the resin which procuded the best elution of the mixture, *i.e.*, narrow elution graphs and high selectivity. This resin was re-used for the succeeding studies.

Flow rate

The same mixture of amines was eluted from Dowex 50-X4 at flow rates of 0.50, 0.75 and 1.00 cm per min. The elution graph (Fig. 1B) for the intermediate flow rate was almost identical with the graph for 0.5 cm per min and was not plotted. A flow rate of about 0.5 cm per min was used in the subsequent work.

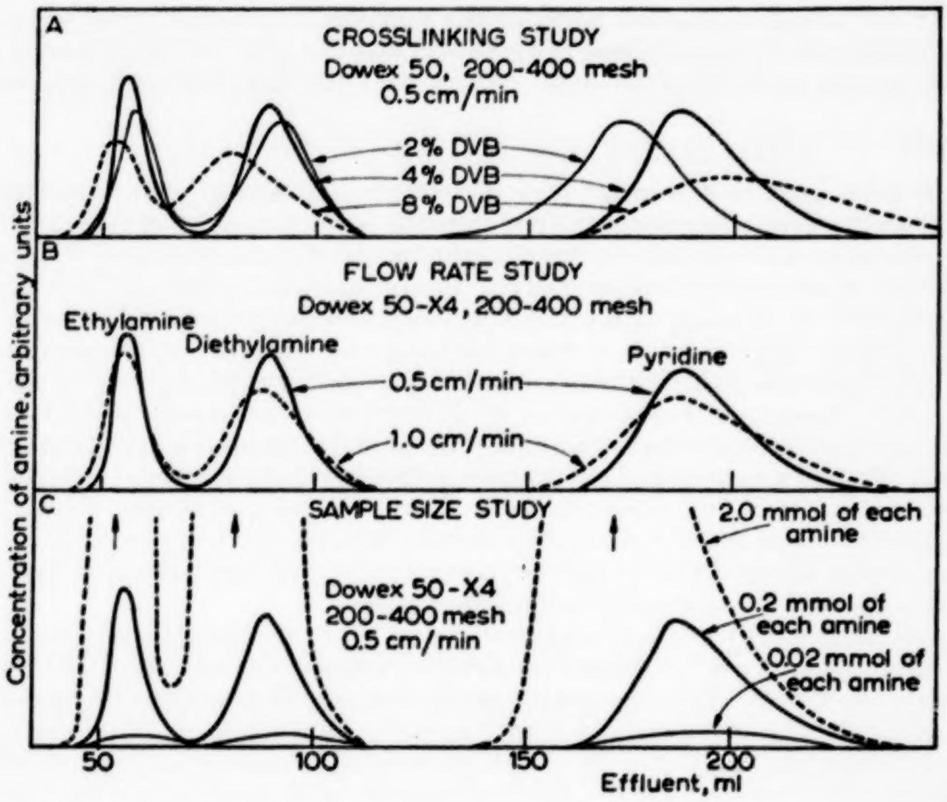

Fig. 1. Variables in salting-out chromatography. The elution of a mixture of ethylamine, diethylamine and pyridine with 0.88*M* potassium phosphate. Dowex 50, 9.7 cm × 3.90 sq. cm, 200-400 mesh.

Sample size

The quantity of amine that may be separated was studied with the same mixture of amines, on Dowex 50-X4 at a flow rate of 0.5 cm per min. With a 100-fold increase in the quantity of amine eluted (Fig. 1C), the leading edge and the peak of the elution graph shift toward the left, whereas the trailing edge remains constant. This effect was noted earlier[5]. For this reason, sample sizes of 0.1 mmole or less were used in the determination of distribution ratios.

Choice of salt

This investigation was begun with eluants of sodium chloride which were 0.1*M* with sodium hydroxide. These eluants showed very little tendency to salt out the amines, whereas eluants of potassium phosphate were more efficient by a factor of 10 and did not require the addition of hydroxide to repress the ion formation by the amine. The potassium salt was chosen because it is very soluble.

Distribution ratios

Each amine investigated was eluted from the potassium form of Dowex 50-X4, 200-400 mesh, 0.5 to 0.75 cm per min, with various concentrations of potassium phosphate as eluant. The distribution ratios C, calculated by equation 1, are given in Table I.

SEPARATION OF AMINE MIXTURES

A plot of the logarithms of the distribution ratios *vs.* the molarity of potassium phosphate is shown in Fig. 2 for several amines. When a mixture of two amines is to

TABLE I

VALUES OF C

No.	*Amine*	*Molarity of potassium phosphate*				
		0.44	0.88	1.32	1.76	2.20
1	Monoethanolamine	1.21	1.69	2.26	3.37	4.84
2	Diethanolamine	1.10	1.56	2.17	3.62	—
3	Triethanolamine	1.58	2.36	3.78	7.01	—
4	Ethylenediamine	1.36	2.08	3.39	7.96	—
5	Diethylenetriamine	1.36	2.31	2.26	13.7	—
6	Triethylenetetramine	1.18	2.29	—	19.2	—
7	Tetraethylenepentamine	1.09	2.34	—	31.7	—
8	Methylamine	1.65	2.23	3.57	6.35	10.34
9	Morpholine	1.69	2.90	5.57	12.4	—
10	Ethylamine	2.02	3.31	6.21	13.0	28.9
11	Isopropylamine	2.51	4.47	9.80	23.1	59.1
12	Tetramethylenediamine	2.84	5.21	12.0	33.0	—
13	*t*-Butylamine	2.82	5.55	12.8	—	—
14	*n*-Propylamine	3.02	5.51	12.4	—	—
15	Diethylamine	3.02	6.09	15.2	—	—
16	*sec*-Butylamine	3.85	8.04	20.5	—	—
17	*n*-Butylamine	5.29	11.2	28.9	—	—
18	Triethylamine	5.07	12.7	37.5	—	—
19	Pyridine	10.0	14.3	29.9	—	—
20	*n*-Amylamine	10.3	23.3	—	—	—
21	Aniline	20.1	29.9	—	—	—
22	Benzylamine	17.5	—	—	—	—
—	*n*-Propyl alcohol	2.27	3.75	6.97	13.9	—

be separated from a column of less than 30 cm, the ratio of C values must be $\geqq$ 1.3 for small monofunctional compounds such as methyl- or ethylamine and $\geqq$ 1.5 for large polyfunctional compounds such as the ethanolamines or the polyethylenediamines. This corresponds to a difference of 0.12 to 0.18 between the curves in Fig. 2. Figure 3 represents the elution of approximately 0.1 mmole of each of these amines in 1 ml of sample. The concentration and the position of eluant changes were calculated prior to the separation by a method previously reported[5]. In this manner, the most efficient separation of a mixture may be determined by use of the data in Table I. The calculated positions of the peaks U^* for the first ten amines were 92.5, 155, 298, 418, 482, 562, 653, 836, 988 and 1065 ml; the observed values of U^* were 90.0, 147, 293, 419, 488, 549, 657, 875, 997 and 1075 ml. The value of U^* for benzylamine was not calculated because of insufficient data (Table I). The ordinate of Fig. 3 refers to (a) the absorbance of Cr(III), produced by the reduction of dichromate by monoethanolamine, (b) the absorbance of benzylamine at 260 mμ measured in 1-cm cells and (c) the milliliters of 0.01M hydrochloric acid used for the titration of the other nine amines included in the separation.

A quantitative separation of a mixture of six additional amines and the corresponding plot of log C are shown in Fig. 4. The ordinate for pyridine[5] and aniline[6] represents one-fifth of the absorbance measured. A small quantity of an impurity present in the sample of aniline was detected between the peaks of pyridine and aniline.

The separation of ethylenediamine and its polymers, shown in Fig. 5, is not quantitative. The elution graphs of these large polyfunctional compounds exhibit a large spread which increases the difficulty of separation. A quantitative separation would

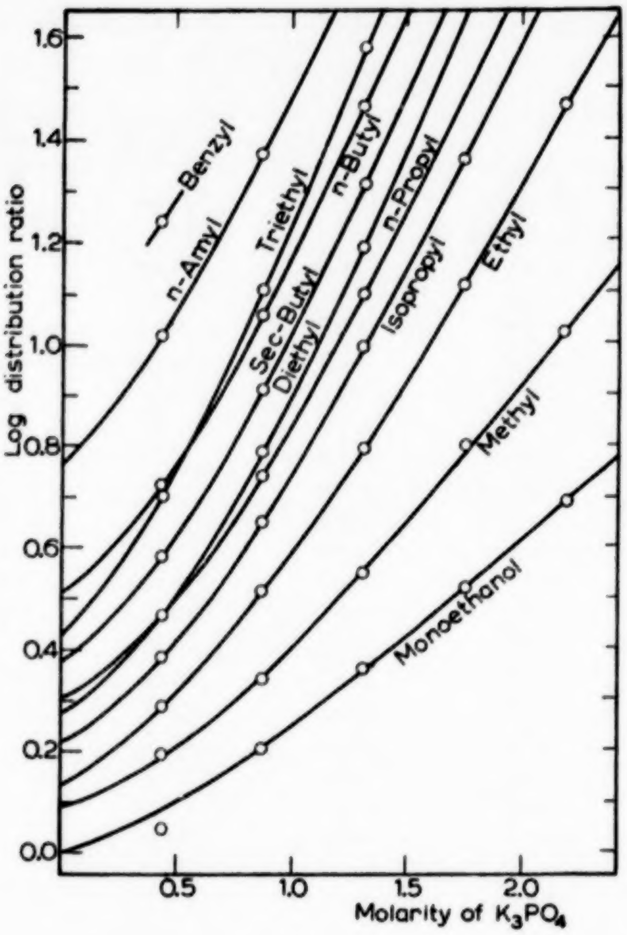

Fig. 2. Log C plots for several amines. Dowex 50-X4, 200-400 mesh.

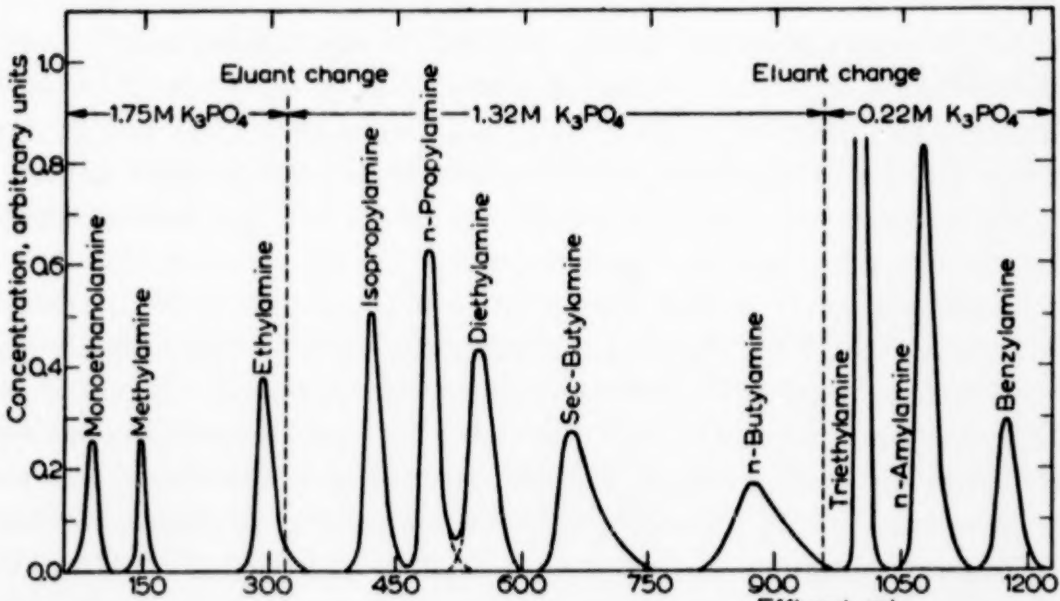

Fig. 3. The separation of an eleven-component mixture. 27.5 cm × 2.28 sq. cm Dowex 50-X4, 200-400 mesh, 0.4 cm per min. Potassium phosphate eluant changed at 324 and 960 ml.

be obtained by elution from a 20-cm column with 1.80M potassium phosphate, but approximately 1 liter of eluant would be required.

The pressure drop through a column of fine-meshed resin causes the flow rate to decrease in proportion to the height of the column. The separations were run at the maximum flow rate that could be obtained with a hydrostatic pressure of 3 ft of eluant.

To increase the flow rate of the 27.5-cm column that was used for the separation in Fig. 3, the finer particles of resin were carefully removed as follows: The resin was slurried with a potassium phosphate solution whose density was slightly less than the density of the resin. The larger resin beads (approximately 200-300 mesh) settled rapidly and were used for the separation.

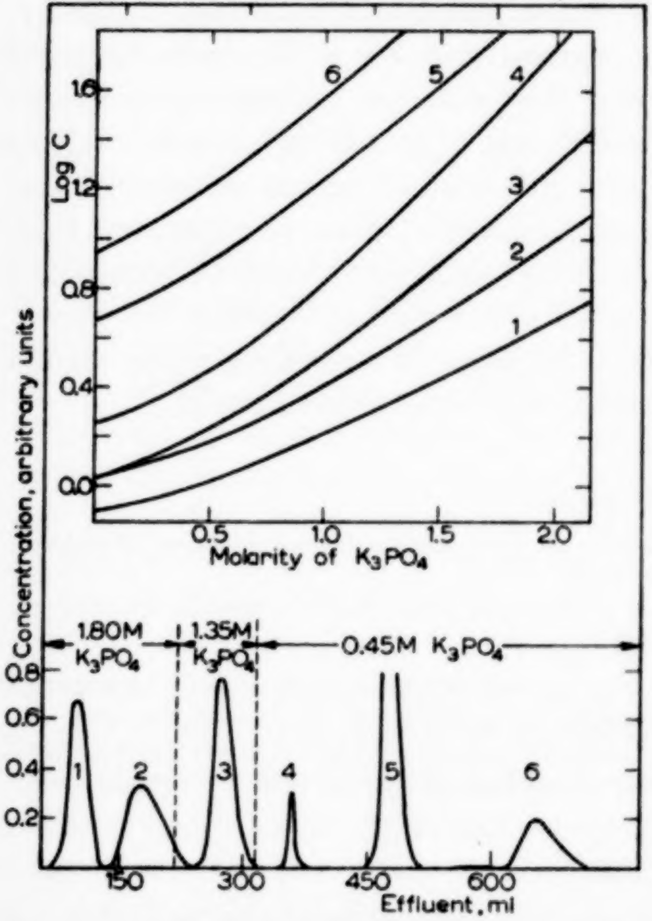

Fig. 4. Log *C* plots (insert) and the separation of a mixture of six amines.
14.4 cm × 3.90 sq. cm Dowex 50-X4, 200-400 mesh, 0.5 cm per min. Potassium phosphate eluant changed at 222 and 318 ml.
1. diethanolamine, 2. triethanolamine, 3. morpholine, 4. tetramethylenediamine, 5. pyridine, 6. aniline.

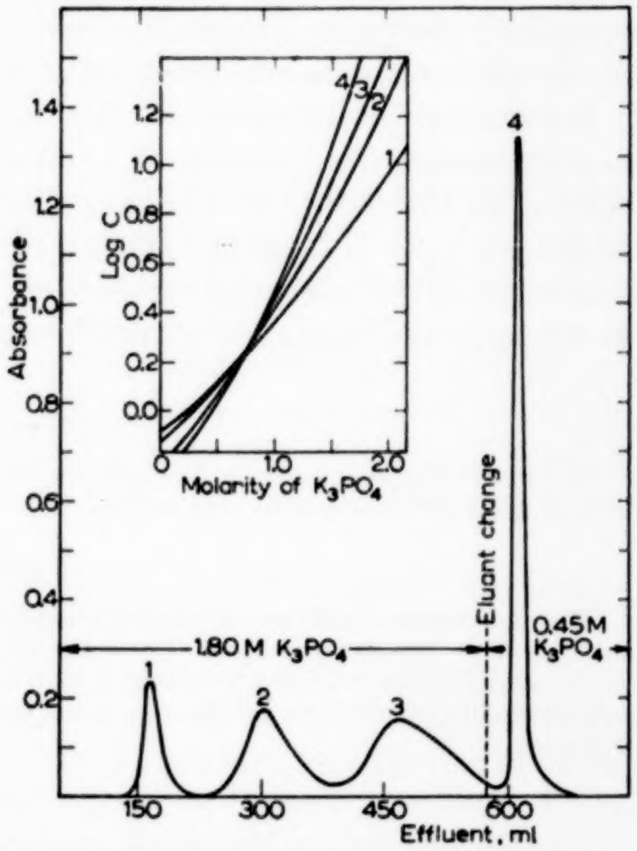

Fig. 5. Log *C* plots (insert) and the separation of ethylenediamine and its polymers.
14.8 cm × 3.90 sq. cm Dowex 50-X4, 200-400 mesh, 0.5 cm per min. Potassium phosphate eluant changed at 576 ml.
1. ethylenediamine, 2. diethylenetriamine, 3. triethylenetetramine, 4. tetraethylenepentamine.

DISCUSSION

In the investigation of the salting-out chromatography of the alcohols[5], the plot of log *C* *vs.* the molarity of the eluant solution for each alcohol was linear and could be represented by the equation

$$\log C = \log C_o + k\,M \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where C_o is the distribution ratio with water as eluant, k is the salting-out constant and M is the molarity of salt in the eluant. The salting-out constant k was shown to be identical with the constant obtained by solubility measurements and the Setschenow equation[5,10].

The plots of log *C* *vs.* *M* for the amines (Figs. 2, 4, 5) are nonlinear with curvature being the greatest for dilute eluants. Curvature is probably caused by the hydrolysis of the tertiary phosphate to yield secondary phosphate and hydroxyl ions. Elutions of *n*-propyl alcohol were run with tripotassium phosphate (Table I), dipotassium hydrogen phosphate and potassium hydroxide of various concentration. The slopes of the log *C* plots were 0.152 for potassium hydroxide, 0.427 for dipotassium hydrogen phosphate and 0.69 for potassium phosphate at high concentrations where the curvature is small. The ratio of the tertiary phosphate that is present in the eluant to the quantity of tertiary phosphate which has been hydrolyzed increases with increasing molarity. The observed curvature is due to the smaller salting-out power of the hydroxide and secondary phosphate ions relative to the tertiary phosphate ion. Salting-out constants for the amines may be estimated from the slope of the log *C* plots at high concentrations.

Because of the similarity of their distribution ratios at all eluant concentrations, *n*-propylamine, *t*-butylamine and tetramethylenediamine cannot be separated from each other by salting-out chromatography. A similar situation occurs for mono- and diethanolamine. It is possible, by the proper chocie of conditions, to effect the separation of all of the other amines listed in Table I. Salting-out chromatography should be useful in the separation of mixutres of amines from biological material.

ACKNOWLEDGEMENT

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SUMMARY

The usefulness of salting-out chromatography to the analysis of amines is illustrated by separations of some complex mixtures. The technique is applicable to primary, secondary, tertiary, aliphatic and atomatic amines. Variables which affect the elution behavior are discussed and a method is provided by which the conditions necessary for the separation of a given mixture may be determined.

RÉSUMÉ

L'utilité de la chromatographie de "salting-out" dans l'analyse des amines est démontrée par la séparation de plusieurs mélanges. La méthode est applicable aux amines primaires, secondaires, tertiaires, aliphatiques et aromatiques. Les variables qui affectent l'élution sont discutées. On discute du choix des conditions les meilleures pour la séparation d'un mélange donné.

ZUSAMMENFASSUNG

Die Nützlichkeit der Aussalzchromatographie in der Analyse von Aminen wird durch die Trennung mehrerer Gemische gezeigt. Primäre, sekundäre und tertiäre Amine der aliphatischen und aromatischen Reihen lassen sich durch diese Technik gut abtrennen. Die veränderlichen Zustände der Elution werden besprochen. Es wird eine Methode beschrieben für die Auswahl der besten Zustände für die Trennung eines angegebenen Gemisches.

REFERENCES

[1] A. T. James, *Biochem. J.*, 52 (1952) 242.
[2] R. Clayton and F. Strong, *Anal. Chem.*, 26 (1954) 579.
[3] H. van Duin, *Biochim. Biophys. Acta*, 12 (1953) 490.
[4] R. Sargent and W. Rieman, *J. Org. Chem.*, 21 (1956) 594.
[5] R. Sargent and W. Rieman, *J. Phys. Chem.*, 61 (1957) 354.
[6] J. Beukenkamp, W. Rieman and S. Lindenbaum, *Anal. Chem.*, 26 (1954) 505.
[7] W. Rieman and S. Lindenbaum, *Anal. Chem.*, 24 (1952) 1199.
[8] R. Sargent and W. Rieman, *Anal. Chim. Acta*, 14 (1956) 381.
[9] H. Smith, *J. Phys. Chem.*, 25 (1921) 231.
[10] I. Setschenow, *Z. physik. Chem.*, 4 (1889) 117.

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PAPER CHROMATOGRAPHY IN THE SEPARATION OF IONS

by

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Application of paper chromatography to the separation of inorganic ions with different solvent mixtures, with or without the help of complexing reagents, was largely due to BURSTALL *et al.*[1] and LEDERER[2]. They recorded the R_F values to show the separability of the ions from a mixture of four or five such ions at the most.

Recently we have attempted the separation of quite a large number of ions by ascending chromatography with a mixture of solvents, acetone, water and hydrochloric acid, in a ratio different from that used by the previous workers and found that with a development period of 18 hours the separation from the following mixtures of all the ions in distinct bands was possible:
Cd-Pb-Cu-Co-Ni, Zn-Cu-Pb-Co-Ni, Hg-Ag-Cu-Pb-Co-Ni, Zn-Mn-Ni, Zn-Co-Ni, Hg-Ag-Pb-Tl, Bi-As, Sb-As, Sn-As, Fe-U-Be-Al or Cr-Th-Zr, Fe-U-Be-Ti-Al-Th-Zr, Fe-U-Be-VO_3^{-1}-Al-Th-Zr, WO_4^{-2}-MoO_4^{-2}, WO_4^{-2}-VO_3^{-1}, VO_3^{-1}-MoO_4^{-2}, VO_3^{-1}-CrO_4^{-2}

During such separations, it has been observed that the distance between the bands of cobalt and nickel and that between copper and lead increase with the rise of room temperature. The R_F values of cobalt and copper increase with the temperature, while that due to lead decreases and for the nickel band the R_F records only a slight increase in value. At lower temperature, the R_F value of lead is greater than that of copper but at higher temperature the reverse is the case, the R_F value of copper is greater compared to that of lead. Again, with the increasing concentration of vanadate the R_L values are found to increase but the R_T values remain practically the same.

EXPERIMENTAL

Apparatus and procedure

The chromatographic development has been carried out by the ascending technique. The apparatus consists of a glass jar closed with a tightly-fitting cork or a rubber bung carrying a clip made of wood. The clip carries a 2.5 cm × 50 cm Whatman No. 1 filter paper strip which is hung to touch the solvent mixture at the bottom of the jar. A convenient volume (about 0.01 ml containing at the most 20 μg of each ion) of the solution to be tested is placed on the centre of the line drawn perpendicularly to the length of the paper, 5 cm above the end of the paper. The wet patch is dried in air for about an hour. After a development period of 18 hours, the strips are taken out, dried in air, and sprayed with a chromogenic reagent, which is not necessarily specific for a particular ion but which is sensitive to a large number of ions to give coloured product.

Solvent, a mixture of "pro-analyse" acetone (40 ml), water (10 ml) and "pro-analyse" hydrochloric acid (*d* 1.124, 5 ml), is kept in the chromatographic jars for 24 hours before being used.

For the tests of the individual cation, a chloride solution of each has been used and for separations of ions from a mixture, the nitrates of Ag, Tl, Hg, Pb, Cu, Cd, UO_2^{+2}, Zn, Mn, Ni and Co, the chlorides of As, Sb, Sn, Bi, Al, Cr, Th, Zr, Ti, Be, Fe, Pd, UO_2^{+2}, ammonium vanadate and molybdate, sodium tungstate and potassium chromate have been utilized.

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Table I gives the R_F values. The effect of temperature on the movements of the bands of Cu, Pb, Co and Ni and the effect of concentration on the movement of vanadate in terms of R_T and R_L values have been recorded in Table II. R_T and R_L represent, respectively, the ratio of the movement of the trailing edge to the solvent front and that of the leading edge to the solvent front.

TABLE I

Ag^{+1}	0.920	As^{+3}	0.785	Al^{+3}	0.211
Hg^{+2}	0.992	Bi^{+3}	0.970	Cr^{+3}	0.255
Pb^{+2}	0.732	Sb^{+3}	0.984	Ti^{+4}	0.291
Zn^{+2}	0.977	Sn^{+2}	0.984	Th^{+4}	0.082
Mn^{+2}	0.347	Pd^{+2}	0.972	MoO_4^{-2}	0.940
Ni^{+2}	0.167	Be^{+2}	0.568	VO_3^{-1}	0.360
Co^{+2}	0.260	ZrO^{+2}	0.017	CrO_4^{-2}	0.970
Cu^{+2}	0.655	UO_2^{+2}	0.944	WO_4^{-2}	0.985
Cd^{+2}	0.943	Fe^{+3}	0.984	Tl^{+1}	0.008

TABLE II

Ions	*Temp. 20-22°C*		*Temp. 34-35°C*		*Temp. 20°C*			VO_3^{-1}
	R_T	R_L	R_T	T_L	R_T	R_F	R_L	
Cu^{+2}	0.62	0.68	0.75	0.81	0.31	0.35	0.38	0.35 µg
Pb^{+2}	0.68	0.75	0.69	0.74	0.30	0.35	0.42	1.4 µg
Co^{+2}	0.22	0.28	0.33	0.38	0.31	0.37	0.44	2.8 µg
Ni^{+2}	0.14	0.20	0.17	0.23	0.30	0.36	0.48	5.6 µg
					0.29	0.36	0.52	11.2 µg

SUMMARY

With a solvent mixture of acetone, hydrochloric acid and water, it is possible to have a thorough separation of ions from each other, in distinct bands, from mixtures containing to a maximum of seven ions. The R_F values of the ions and the effect of temperature and concentration on the R_T and R_L values have been recorded.

RÉSUMÉ

Avec un mélange des solvants suivants: acetone, acide hydrochlorique et eau, il est possible d'avoir une séparation complète en ions, en bandes distinctes, de mélanges contenant jusqu'à un maximum de sept ions. Les valeurs R_F des ions et l'effet de la température et de la concentration sur les valeurs R_T et R_L ont été trouvés.

ZUSAMMENFASSUNG

Mit einem Lösungsmittelgemisch von Aceton, Salzsäure und Wasser kann man die Ionen von Gemischen die bis zu 7 verschiedene Ionen enthalten in deutliche Bänden trennen. Die R_F-Werte der Ionen und die Einflüsse von Temperatur und Konzentration auf die R_T und R_L-Werte wurden festgestellt.

REFERENCES

[1] F. H. Burstall, G. R. Davies, R. P. Linstead and R. A. Wells, *Nature*, 163 (1949) 64; *J. Chem. Soc.*, (1950) 516.

[2] E. Lederer and M. Lederer, *Chromatography*, Elsevier Publishing Co., 2nd Ed., Amsterdam, 1957.

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DÉTERMINATION CONTINUE DU CARBONE-14 ET DU SOUFRE-35 EN MILIEU AQUEUX PAR UN DISPOSITIF A SCINTILLATION

APPLICATION AUX EFFLUENTS CHROMATOGRAPHIQUES

par

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INTRODUCTION

La faible énergie des électrons émis par le carbone-14 et le soufre-35 constitue une des principales difficultés rencontrées lors de la mesure de ces isotopes dans les milieux biologiques. Le parcours maximum de ces particules est en effet de l'ordre de 0.3 mm pour un milieu de densité unitaire (30 mg/cm^2), de sorte que celles-ci sont rapidement absorbées soit par le milieu ambiant, soit par la paroi des compteurs.

Les compteurs à fenêtre mince et sans fenêtre permettent d'effectuer des déterminations satisfaisantes pour autant que l'échantillon puisse être amené à un poids réduit de matière et qu'il soit tenu compte de la correction d'auto-absorption. De nombreuses manipulations sont néanmoins nécessaires pour amener l'élément radioactif sous une forme chimique définie et pour obtenir, par un étalement uniforme, une géométrie reproductible.

Le carbone-14 peut éventuellement être dosé en phase gazeuse; cette technique, bien que la plus efficace, est malheureusement très complexe.

Dans le cas particulier des effluents chromatographiques le nombre souvent très élevé de fractions à analyser multiplie encore les manipulations dans des proportions excessives.

Pour cette raison, nous avons recherché une technique de mesure applicable directement aux milieux liquides. Deux méthodes ont été utilisées jusqu'à présent dans ce but:

(1) l'étalement en couche mince,

(2) les scintillateurs liquides.

Le premier de ces principes a été appliqué récemment par BANGHAM[1] pour l'estimation continue des rayons β mous dans les effluents chromatographiques. Cet auteur a pu améliorer la géométrie du compteur GM à fenêtre mince en faisant circuler le liquide au contact d'une paroi de mica de grande dimension (37.5 cm^2). Le rendement obtenu est de 1% environ pour une capacité de 1.5 ml.

L'utilisation de scintillateurs liquides résout de façon très élégante le problème de l'auto-absorption. Même dans le cas d'un rayonnement aussi faible que celui du tritium des rendements appréciables ont été obtenus. Malheureusement cette technique n'apporte aucune solution simple pour une méthode continue de dosage.

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L'appareil que nous avons élaboré pour l'analyse continue des effluents chromatographiques[2] est basé sur l'étalement du liquide au contact de plastique scintillant et comprend deux parties distinctes que nous décrirons successivement.

CELLULE SCINTILLANTE

Étude des caractéristiques

Vu le parcours maximum des particules à doser, une épaisseur liquide supérieure à 0.3 mm n'apporte aucune augmentation de la radioactivité décelable et ne contribue donc qu'à augmenter le volume de la cellule. Des raisons mécaniques (fraisage, résistance à l'écoulement) nous ont incités initialement à ne pas diminuer cette épaisseur, d'autant plus que la surface totale imposée par la zone sensible des photomultiplicateurs (PM) employés, nous fournissait ainsi un volume de 0.8 ml. Ce volume se rapproche favorablement de celui des fractions utilisées en chromatographie et est compatible avec le degré de résolution obtenu par cette méthode. Il ressort toutefois de nos essais que des épaisseurs moindres sont parfaitement réalisables et n'entraînent pas d'élévation excessive de la résistance à l'écoulement. Pour un volume défini, une augmentation considérable du rendement pourrait ainsi s'obtenir par l'accroissement de la surface efficace, grâce notamment à l'emploi soit d'un photo-multiplicateur à grande photo-cathode (EMI 6099) ou d'un système optique adapté.

Le choix du volume n'a bien entendu de sens que si la résolution chromatographique n'est pas compromise par une diffusion au sein du liquide, ce que nous avons pu obtenir par le dispositif en ,,ruban" décrit plus loin.

Les réflexions risquant de diminuer le rendement lumineux sont écartées au maximum en évitant les surfaces cylindriques ou sphériques. Toutes les interfaces sont parallèles à la photocathode des PM afin d'augmenter l'angle d'incidence des rayons lumineux.

Description (Fig. 1 et 2)

La cellule assemblée présente extérieurement l'aspect d'un cylindre de 65 mm de diamètre et de 25 mm de hauteur, contre les bases duquel s'appliquent les photo-cathodes de deux PM. Le canal de 0.3 × 4 mm dans lequel circule le liquide est formé par l'accolement de deux lames scintillantes (A, A') contre les épaulements de 0.5 mm de large fraisés dans la plaque médiane en plexiglas (B). Celle-ci n'est pas usinée sur les tranches. Deux pièces latérales (C, C') assurent la continuité des épaulements d'une face à l'autre et son maintenues en contact étroit par les vis (D). Ces différentes parties sont enchassées dans deux flasques en plexiglas (E, E') qui en assurent l'assemblage et l'étanchéité, grâce au serrage des vis (F).

La Fig. 2 montre en coupe le dispositif de connexion prévu pour l'entrée et la sortie du liquide et prenant place en (G, G') dans la flasque (E). Une aiguille hypodermique (H) de 1 mm de diamètre extérieur est introduite par (L) jusqu'au niveau du canal, à travers une rondelle en caoutchouc (J) qui, comprimée par le bouchon fileté (K), assure l'étanchéité de la connexion. Grâce à leur courbure en S aucune lumière ne peut accéder par les aiguilles à la zone sensible.

Les lames scintillantes (A, A') sont en plastique NE 101 livré par le fabricant (Nuclear Enterprises Ltd., Winnipeg, Canada) en 0.3 mm d'épaisseur. Celle-ci correspond, comme celle du liquide, au parcours maximum des rayons à mesurer. Une épaisseur plus grande ne pourrait donc qu'élever le ,,background".

De l'huile de silicone garantit un couplage optique efficace entre les pièces (A, A') et (E, E').

La disposition et la configuration de toutes les pièces ont été étudiées pour favoriser le démontage et le nettoyage aisés, l'accessibilité parfaite au polissage et l'absence de zones stagnantes sur le parcours du liquide.

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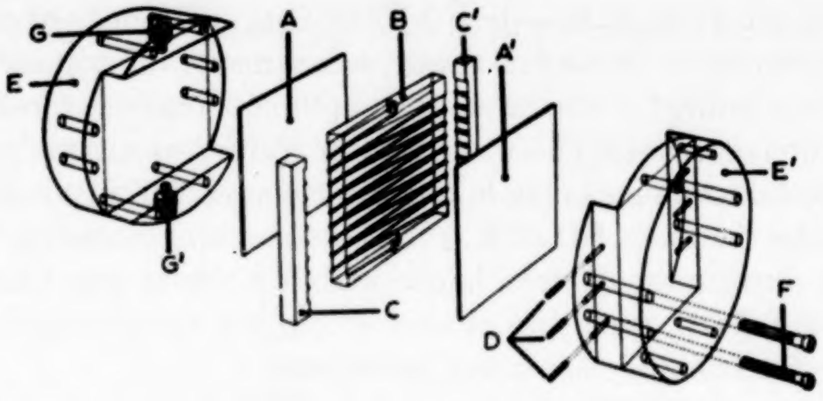

Fig. 1. Vue exposée de la cellule scintillante.

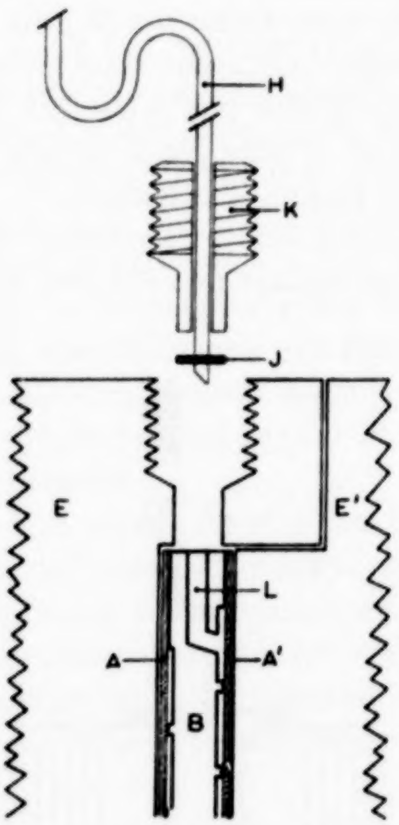

Fig. 2. Dispositif de connexion pour l'entrée et la sortie du liquide (coupe perpendiculaire au plan d'écoulement du liquide).

ÉQUIPEMENT ÉLECTRONIQUE

L'élément scintillant est placé entre deux cellules photomultiplicatrices EMI 6260 B. Le couplage optique est assuré par de la pâte de silicone (Wacker-Chemie) et le tout placé dans un blindage d'acier de 5 cm d'épaisseur. Deux préamplificateurs de rapport 1 : 1 (MBLE, PN 240/c) sont accolés aux cellules et complètent l'ensemble détecteur. Toutes les mesures sont effectuées à la température ambiante ; toutefois une circulation d'air est prévue pour dissiper les calories dégagées principalement par les tubes des préamplificateurs.

Les impulsions de sortie sont envoyées à deux amplificateurs à large bande (IDL, type 652) et de là vers un circuit de coïncidence[3]. Un intégrateur associé à un enregistreur complète le montage.

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La stabilité et la précision du moniteur AIRMEC 1021 B nous ont permis d'utiliser celui-ci comme intégrateur. Toutefois il est nécessaire de lui adjoindre un dispositif automatique de changement d'échelle assez compliqué à réaliser. C'est pourquoi nous avons actuellement porté notre choix sur un intégrateur logarithmique MBLE.

L'adaptation de l'impédance entre le circuit de sortie de l'intégrateur (100 μA) et l'enregistreur à cadre (Siemens, SD 12 K, 1 mA) est aisément réalisée grâce au montage transformateur d'impédance de très haute stabilité décrit par CERF ET LIBERT[4]. L'alimentation THT (IDL, type 532) et tous les circuits électroniques sont alimentés par un régulateur électronique de tension SØRENSEN.

CARACTÉRISTIQUES DE FONCTIONNEMENT (FIG. 3)

L'appareil décrit est utilisé pour la mesure de la radioactivité dans les effluents de colonnes d'échangeurs d'ions du type utilisé par MOORE ET STEIN[5]. Dans ce but l'ensemble scintillant est intégré entre la colonne et un collecteur de fractions à siphon[6]. A une pression d'eau de 2-3 cm, réglable par la hauteur de l'entonnoir, correspond un débit de 20 ml/h. Chaque fraction débitée par le siphon commande l'inscription d'un trait sur le graphique, ce qui en facilite le repérage.

L'observation visuelle au moyen de solutions colorées et l'allure comparée des courbes chromatographiques avec et sans passage de l'effluent dans la cellule, confirment l'ab-

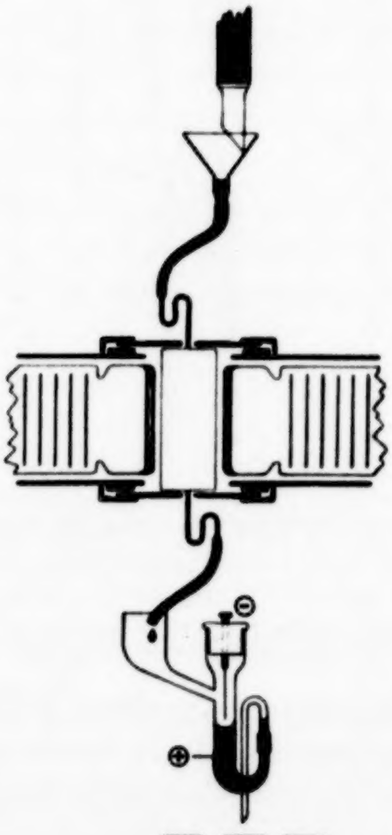

Fig. 3. Montage de la cellule scintillante pour la mesure de la radioactivité dans les effluents chromatographiques. Pour la clarté du dessin, les aiguilles sont représentées verticales alors qu'elles sont en réalité situées dans un plan horizontal.

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TABLEAU I

ACTIVITÉS ENREGISTRÉES DANS L'EFFLUENT AU COURS DE LA CHROMATOGRAPHIE D'UN ECHANTILLON DE TAURINE-^{35}S SUR DOWEX 50

Fraction no.	*Activité c/min*	*Fraction no.*	*Activité c/min*
1	0	8	10.000
2	120	9	6.600
3	420	10	2.520
4	960	11	240
5	2.200	12	60
6	7.800	13	0
7	18.000		

Activité max. atteinte: 24.000 c/min

sence quasi totale de diffusion. Ce fait est aussi illustré par les valeurs du Tableau I se rapportant à la chromatographie d'un échantillon de taurine-^{35}S. Malgré son activité relativement élevée aucun retard n'est observé lors du retour au ,,background".

Jusqu'à présent notre appareil a fonctionné avec un rendement de 5 à 6%. Celui-ci se compare donc favorablement à celui qui serait obtenu en mesurant le contenu de la cellule au moyen d'un compteur GM à fenêtre mince, après évaporation du solvant et en l'absence d'auto-absorption. La mesure en milieu liquide offre encore cet avantage sur l'évaporation, que le rendement n'est que peu affecté par la présence de sels dans l'éluant, ceux-ci ne modifiant pas sensiblement la densité du milieu dont dépend l'auto-absorption. La lecture du graphique permet de déceler des pics équivalant à une radioactivité de quelques millimicrocuries.

La présente méthode allie à sa sensibilité et à son automatisme, l'intérêt de n'être pas destructive. La possibilité de récupérer les corps radioactifs décelés dans l'effluent en vue de manipulations ultérieures nous a notamment permis d'effectuer plusieurs chromatogrammes d'un même échantillon dans des conditions variées pour en améliorer la séparation. En outre, la superposition des diagrammes de radioactivité aux résultats obtenus par voie chimique sur le même effluent, procure un moyen pratique d'identification (Fig. 4).

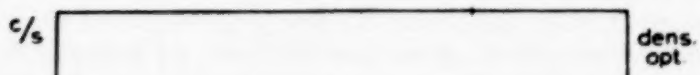

Fig. 4. Chromatographie de taurine-^{35}S sur Dowex-50. ———: enregistrement de la radioactivité dans l'effluent. - - - - -: courbe correspondant à l'analyse chimique par le réactif à la ninhydrine suivant la méthode de MOORE ET STEIN[7], après passage de l'effluent au travers de la cellule scintillante.

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Bien qu'équipé pour des déterminations continues, le montage décrit permet aussi l'emploi de cellules scintillantes pour la détermination discontinue de la radioactivité dans les milieux aqueux en général. Dans un cas comme dans l'autre l'emploi de telles cellules garantit une géométrie constante lors des mesures.

REMERCIEMENTS

Certaines parties de notre montage ont été effectuées dans les ateliers de mécanique du Professeur Baudoux que nous tenons à remercier très sincèrement de même que ses collaborateurs, Messieurs Picciotto et Hirschberg, avec qui nous avons eu de fructueux entretiens.

La réalisation de la cellule scintillante a pu être menée à bonne fin grâce aux judicieux conseils et à la précision du travail de Monsieur Ockum.

Nous exprimons aussi notre reconnaissance à Monsieur B. Grinberg, du Commissariat à l'Énergie Atomique (France), pour l'initiation personnelle dont il a fait bénéficier l'un de nous (R.L.) dans le domaine des scintillateurs.

RÉSUMÉ

Un appareil enregistreur est décrit pour la mesure des rayons peu pénétrants (^{14}C, ^{35}S) en milieu aqueux, spécialement adapté pour l'analyse continue des effluents chromatographiques. Il est basé sur l'étalement du liquide en couche mince au contact d'un scintillateur plastique associé à un montage en coïncidence. Son rendement est comparable à celui qu'aurait un compteur GM à fenêtre mince en l'absence d'auto-absorption.

SUMMARY

A recording apparatus is described for determining soft radiations (^{14}C, ^{35}S) in aqueous medium, especially adapted for continuous analysis of chromatographic effluents. It is based upon the spreading of the liquid in a thin layer in contact with a plastic scintillator coupled to a coincidence circuit. The efficiency is comparable to that of a thin end-window GM counter in the absence of auto-absorption.

ZUSAMMENFASSUNG

Ein Registrierapparat zur Messung wenig durchdringender Strahlen (^{14}C, ^{35}S) in wässrigem Milieu wird beschrieben; er ist speziell zur kontinuierlichen Analyse chromatographischer Eluate ausgestattet. Die Flüssigkeit wird hierbei in einer dünnen Schichte ausgebreitet. Die Ausbeute des Apparates ist vergleichbar mit derjenigen einer GM-Zählers mit dünnem Fenster ohne Auto-Absorption.

BIBLIOGRAPHIE

[1] D. R. Bangham, *Biochem. J.*, 62 (1956) 552.
[2] E. Schram et R. Lombaert, *Biochem. J.*, 66 (1957) 8 p.
[3] J. Fischer et J. Marshall, *Rev. Sci. Instr.*, 23 (1953) 417.
[4] J. Cerf et Ch. Libert, *Arch. intern. physiol. et biochem.*, 63 (1955) 376.
[5] S. Moore et W. H. Stein, *J. Biol. Chem.*, 192 (1951) 663.
[6] E. Schram et E. J. Bigwood, *Anal. Chem.*, 25 (1953) 1424.
[7] S. Moore et W. H. Stein, *J. Biol. Chem.*, 211 (1954) 907.

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FAST GREY RA AS A NEW COLORIMETRIC REAGENT. MICRO-DETERMINATION OF MOLYBDENUM

by

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This investigation was undertaken to ascertain the feasibility of the spectrophotometric micro-determination of molybdenum. The reaction between molybdenum and the sulphonic acid azo-dye Fast Grey RA in a moderately acid acetone-water mixture has been chosen for this application. Published methods of the colorimetric determination of molybdenum in most cases involve either extraction of the coloured complex or a long procedure. Even the most important thiocyanate method[1], stated to be the most reliable for trace molybdenum analysis[2], or the dithiol method[3] has some draw-backs[1] such as low stability, extraction of the coloured complex, interference of coloured substances and low sensitivity. The present method is simple and rapid and provides for the elimination of most of the above-mentioned interferences.

EXPERIMENTAL

Compounds. The materials used either for preparing the molybdenum solution or as interfering elements, were all of the required purity. These included ammonium molybdate, acetone, nitrates of copper, bismuth, calcium, magnesium, barium, cobalt, aluminium, thorium, silver, mercury(I), chlorides of antimony, zinc, manganese, ferric iron, lead acetate, sulphates of nickel, cadmium and ammonium, zirconium oxychloride, chlorate, acetate, fluoride and formate of sodium, citric, phosphoric, tartaric and oxalic acids. The water used was always distilled twice.

Solutions. The molybdenum solution is prepared by dissolving 0.4602 g of a previously dried A.R. grade ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of H_2O (1 ml = 0.5 mg Mo). The molybdenum content was checked by the sulphide method[4]. A stock solution containing 100 g Mo per ml is prepared by appropriate dilution from the standardized molybdenum solution. Further dilution is prepared from this stock solution.

Solutions containing 0.5 mg per ml of each of the above-mentioned cations and anions are prepared by dissolving, whenever possible, the calculated amounts in the required volume of water.

The reagent solution: 0.1 g of the dye is dissolved in 100 ml of H_2O.

Effect of pH. Since Fast Grey is a sulphonic acid azo-dye, *i.e.* a weak acid, its dark violet aqueous solution is easily converted into a faint orange solution in a fairly acid medium. By developing the light purple colour of the molybdenum-Fast Grey compound in different acidities using 0.02 to 0.1*M* nitric or hydrochloric acid solutions, it was concluded that the best colour is developed in 2 ml of 0.05*M* acid per 10 ml.

Effect of alcohol and acetone. By developing the colour of the Fast Grey-molybdenum compound in solutions made up of 40% alcohol or acetone it was found that alcohol is without any appreciable influence, whereas a pronounced increase in the intensity of the colour is observed in the acetone-water medium.

Selection of the suitable wavelength. With the aid of a recording Beckman spectrophotometer it was been found that the maximum absorbancy of the molybdenum-Fast Grey compound is at a wavelength of 570 mμ.

Molecular structure of the molybdenum-Fast Grey compound. Fast Grey is an azo-dye with the constitutional formula $C_{16}H_{11}O_7N_3S$. The molecular structure of its compound with molybdenum was investigated by carrying out measurements with solutions containing 50 μg Mo per 10 ml + 2 ml of 0.05 M HCl acid solution + increasing volumes of 0.1% reagent + water up to 10 ml in volumetric flasks, against pure water as the blank, using a Beckman spectrophotometer type B with a blue sensitive photocell and 1 cm cells at a wavelength of 570 mμ. Representative results are listed in Table I.

TABLE I

ml 0.1% reagent	0.8	1	1.1	1.2	1.3	1.4	1.5
Transmittancy	32.5	29.0	27.3	26.0	25.5	24.0	22.5
Absorbancy	0.49	0.54	0.565	0.585	0.59	0.61	0.625

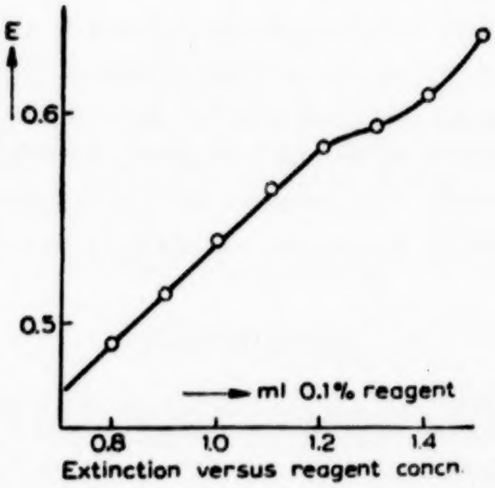

Fig. 1

From the above data and the corresponding Fig. 1, it is apparent that the volume of 0.1% reagent required to react quantitatively with 50 μg Mo is 1.2 ml, from which the molecular weight of the dye was calculated to be 384 if it were monobasic. This was verified in experiments. The agreement of the latter value with the exact molecular weight of 389.33 suggests a molecular structure of one mole of molybdenum and six moles of the dye.

Sensitivity and sequence of additions. With the aid of such a sensitive instrument as the Langé photometer it is possible to determine 0.1 p.p.m. of Mo in pure aqueous solutions or 0.05 p.p.m. in an acetone-water medium. It is also easily possible to determine 0.2 p.p.m. of Mo with a Beckman spectrophotometer.

By varying the sequence of additions of the constituents, in the presence of which the coloured F.G.-Mo compound is produced, it was concluded that the best sequence is the following one: Mo-acid-reagent-acetone and water.

Effect of time. The absorbancy of a series of solutions involving 10 to 100 μg Mo per 10 ml (Mo solution + 2 ml 0.05 M HCl + 2.5 ml of 0.1% reagent + 4 ml of pure acetone

+ water up to 10 ml) was recorded 15, 60 and 180 minutes after preparation. The values in Table II were recorded 15 minutes after preparation but remained almost constant for the entire length of the above periods.

TABLE II

μg Mo	10	20	30	40	60	80	100
Transmittancy	79.5	62.0	48.0	37.0	22.5	13.5	8.0
Absorbancy	0.106	0.207	0.32	0.43	0.65	0.87	1.1

Influence of temperature: Measurements can be carried out between 15° and 30°C without any appreciable deviations.

Influence of foreign ions. We proceeded to investigate the problem of the interfering elements systematically by measuring the transmittancy of solutions containing 20 μg Mo + at least 200 μg of the previously mentioned cations per 10 ml. In some cases where higher interferences were expected, less than 10-fold the Mo-amount was used (Cu^{+2}, Zr, V, Bi, 50 μg). Special procedures were applied with cations of Pb, Sb and Sn^{+2}. It is worthy to notice that in most cases where a precipitate was formed, following addition of the reagent (Fe^{+3}, Al, Hg^{+}, R.E's[*,5], Ca, Pb), a clear solution was obtained after addition of the acetone solution. The results are listed in Table III.

TABLE III

Solution	*Transmittancy* %	*Solution*	*Transmittancy* %	*Solution*	*Transmittancy* %
20 μg Mo	61.5	20 μg Mo + Cd	61.0	20 μg Mo + Cu^{+2}	1.5
,, + Mg	61.5	,, + Al	63.5[6]	,, + Fe^{+3}	9.0
,, + Zn	61.0	,, + Hg^{+}	54.5†	,, + Mn	61.7
,, + Bi	40.0	,, + Cr	66.0	,, + Sb	68.0
,, + R.E's	61.0	,, + Ag	58.0	,, + Pb	55.0
,, + Th	58.0	,, + Ni	57.5	,, + V	10.0
,, + U	26.5	,, + Sn^{+2}	66.0	,, + Ba	62.0
,, + Ca	63.0	,, + Zr	11.5	,, + Co	61.5

† Solution slightly turbid.

These results indicate that, with few exceptions, the highly interfering elements are ferric iron, vanadium, copper and bismuth.

We succeeded, to an appreciable extent, to exclude the ferric iron interference by adding 0.1 ml of 0.4*M* ascorbic acid solution to the mixture of Mo + Fe^{+3} solution, whereby the dark brown colour due to ferric iron no longer appears. A solution containing 20 μg Mo + 200 μg Fe^{+3} after the above treatment, recorded a transmittancy of 60%, whereas with 400 μg Fe^{+3} the transmittancy amounted to 54% as compared with 9% in the absence of ascorbic acid.

In the case of copper we were only able to exclude most of the interference due to one-fold the molybdenum amount of 20 μg, by adding 0.1 ml of 0.4*M* ascorbic acid solution + 0.1 ml of 2*M* NH_4CNS solution. Such a solution recorded a transmittancy of 56 as compared with 1.5% before the above treatment.

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[*] A mixture of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Cp.

By applying a same procedure for testing the interference of the anions previously mentioned it is concluded that the presence of almost all these anions in at least 10 fold the Mo-amount do not interfere with its determination, provided the acidity of the test solution is the same as that of pure Mo-solution.

Obeyance of Beer's law. Two sets of measurements are carried out, one covering the range of 0.05 to 1 p.p.m. of Mo using the Langé photometer, and the other covering the range of 1 to 10 p.p.m. using the Beckman spectrophotometer. Both sets of measurements, whether carried out in purely aqueous solutions or in acetone-water mixtures, indicate that the variation of concentration with extinction conforms quite satisfactorily with Beer's law. A third set of measurements which proved the validity of Beer's law was carried out with solutions involving the range of 0.2 to 1 p.p.m. of Mo using the Beckman instrument. The results are represented graphically by the curves A, A', B, B' and C in Figs. 2-4.

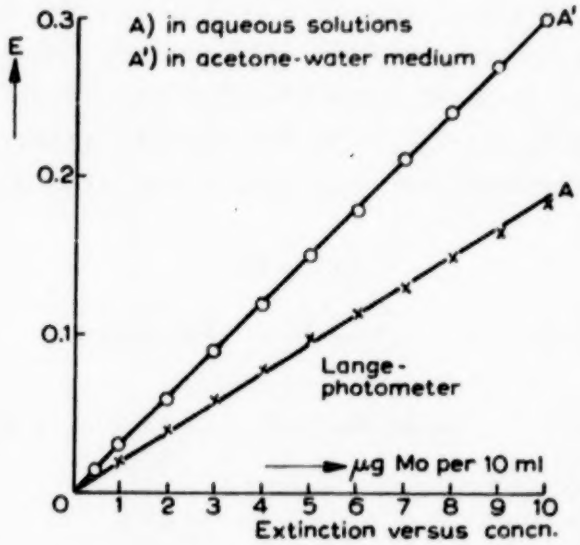

Fig. 2

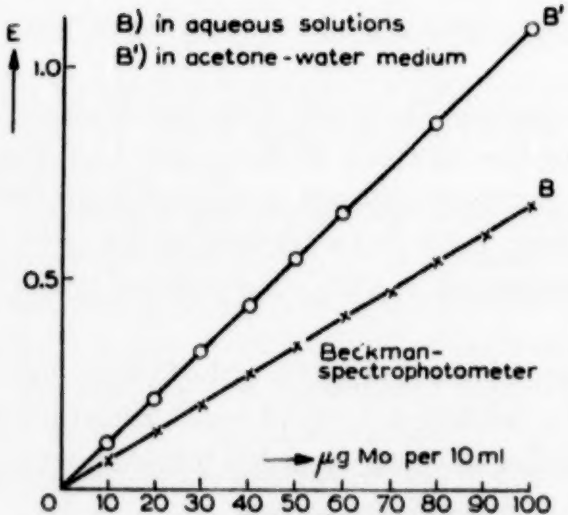

Fig. 3

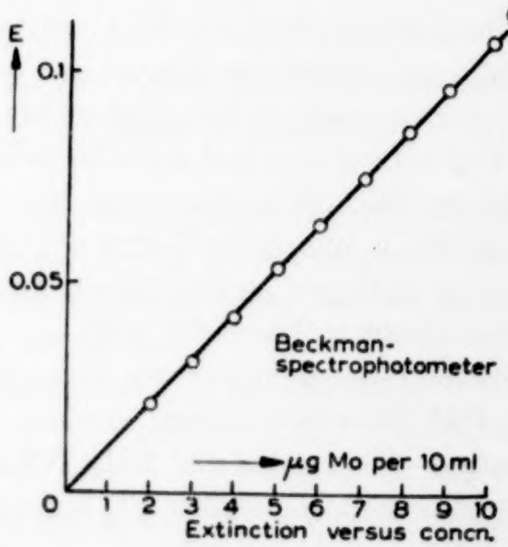

Fig. 4

Procedure. With pure molybdenum, 1 ml containing from 0.05 to 1 p.p.m. (low range) or 1 to 10 p.p.m. (high range) is transferred to a 10 ml flask. The reagents are pipetted into the flask in the following order mixing after each addition: 2 ml of 0.05*M* HCl acid solution, 2.5 ml of 0.01% (with the low Mo range) or 2.5 ml of 0.1% freshly prepared reagent solution (with the high Mo range), 4 ml of acetone and finally water up to the mark. With Mo solutions containing up to 200 μg Fe^{+3} or 20 μg Cu^{+2} the solutions are evaporated to dryness on a water bath, the residue dissolved in 1 ml of 0.1*M* HCl acid solution and transferred with 2 ml of water into a 10 ml flask. 0.1 ml of 0.4*M* ascorbic acid solution is then added to mask ferric iron or the same amount of ascorbic acid, and 0.1 ml of 2*M* NH_4CNS solution to mask cupric ions, followed by the reagent and acetone solutions. The absorbancy is measured against a blank containing the same constituents but without Mo, using a sensitive photometer and orange filters with maximum absorbancy at 570 mμ with the low Mo range, or a Beckman instrument at the same wavelength with both Mo ranges of 0.2 to 1 or 1 to 10 p.p.m. The concentration of Mo can be read from curves prepared in the same manner from standard Mo solutions (Figs. 2-4). The colour under these conditions is developed within 15 minutes and is stable for a considerable period of time.

SUMMARY

Fast Grey RA dye has proved to be a suitable colorimetric reagent for the determination of molybdenum amounts covering the micro-range of 0.05 to 10 p.p.m. in an acetone-water medium. Beer's law is proved to be valid through the whole range. Serious interferences are due to Fe^{+3}, Cu^{+2}, Zr, V and Bi. Ferric iron up to 200 μg per 10 ml is masked with ascorbic acid, whereas cupric ion up to 20 μg per 10 ml is masked with ascorbic acid and ammonium thiocyanate solutions.

RÉSUMÉ

Le colorant appelé ,,Fast Grey RA" se révèle comme un bon réactif colorimétrique pour la détermination de quantités de molybdène de l'ordre de grandeur de 0.05 à 10 parties par million (p.p.m.), en milieu acétone-eau. La loi de Beer est valable dans l'intervalle donné. De sérieuses interférences sont dues au Fe^{+3}, Cu^{+2}, Zr, V et Bi. L'ion ferrique jusau'à 200 μg par 10 ml est masqué avec de l'acide ascorbique, tandis que l'ion cuivre(II) jusqu'à 20 μg par 10 ml est masqué par des solutions d'acide ascorbique et de thiocyanate d'ammonium.

ZUSAMMENFASSUNG

Der Farbstoff Echtgrau RA (,,Fast Grey Ra") hat sich als ein geeignetes kolorimetrisches Reagenz zur Bestimmung von Molybdän in Mengen von 0.5 bis 10 Teilen pro Million in Aceton-Wasser erwiesen. Das Beer'sche Gesetz ist in dem ganzen Bereiche erfüllt. Es stören: Fe^{+3}, Cu^{+2}, Zr, V, und Bi. Dreiwertiges Eisen bis zu 200 μg pro 10 ml wird mit Ascorbinsäure, zwiewertiges Kupfer bis 20 μg pro 10 ml mit Ascorbinsäure und Ammoniumthiocyanatlösungen maskiert.

REFERENCES

[1] E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Ed., Interscience Publishers, Inc., New York and London, 1950, p. 455.

[2] W. F. HILLEBRAND, G. E. F. LUNDELL, H. A. BRIGHT AND J. E. HOFFMAN, *Applied Inorganic Analysis*, John Wiley & Sons, Inc., 2nd Ed., New York, 1953, p. 314.

[3] C. F. BICKFORD, W. S. JONES AND J. S. KEENE, *J. Am. Pharm. Assoc.*, Sci. Ed., 37 (1948) 255.

[4] J. W. MELLOR AND H. V. THOMPSON, *A Treatise on Quantitative Inorganic Analysis*, 2nd Ed., Chas. Griffin & Co., Ltd., London, 1938, p. 446.

[5] F. HECHT, J. KORKISCH, R. PATZAK AND A. THIARD, *Mikrochim. Acta*, 7-8 (1956) 1288.

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THE THERMAL DECOMPOSITION OF THE 5,7-DIHALO-8-QUINOLINOL RARE EARTH METAL CHELATES

by

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The rare earth metal ions form slightly soluble chelates with 8-quinolinol which have proven useful in analytical chemistry[1,7]. The differences in incipient pH values for precipitation has enabled various separations from associated metal ions to be made[2-5]. The normal formula for the chelates is $M(C_9H_6NO)_3$, where M is the rare earth metal ion. In the case of cerium, air oxidation forms a chelate with the metal ion in a higher oxidation state corresponding to the formula, $Ce(C_9H_6NO)_4$[7,9]. Under certain conditions, such as a tartrate buffer[3] or by homogeneous precipitation[8], the trivalent cerium chelate can also be obtained.

Little work has been done on the rare earth metal chelates with the substituted 8-quinolinols. The 5,7-dichloro-8-quinolinol chelates of neodymium and erbium have been investigated spectrophotometrically[6]. Difficulty was experienced by these authors in obtaining stoichiometric chelates except under very careful experimental conditions. The thermal decomposition of the 2-methyl-8-quinolinol[10] and 5,7-diiodo-8-quinolinol[11] chelates has recently been studied on the thermobalance. It was found that the thermal stability of these chelates was much lower than the corresponding unsubstituted 8-quinolinol chelates[8].

From the existing data on the thermal decomposition of the substituted 8-quinolinol metal chelates, it appears likely that other substituted 8-quinolinol chelates would probably exhibit lower thermal stabilities. Thus, the object of this investigation was to study the variation in thermal stability of the rare earth metal chelates with substitution on the 8-quinolinol molecule. To do this, the rare earth chelates with 5,7-dichloro-8-quinolinol (DCQ), 5,7-dibromo-8-quinolinol (DBQ) and 5,7-diiodo-8-quinolinol (DIQ) were prepared and subjected to thermal decomposition on the thermobalance.

EXPERIMENTAL

Reagents. 5,7-Dichloro-8-quinolinol (melting point 177-9°C) was obtained from Eastman Organic Chemicals Co., Rochester 3, N. Y. 5,7-Dibromo-8-quinolinol (melting point 195-6°C) was obtained from Matheson, Coleman and Bell Co., East Rutherford, N. J. 5,7-Diiodo-8-quinolinol (melting point 208-10°C) was obtained from the Aldrich Chemical Co., Inc., Milwaukee 12, Wisc.

The sources of the rare earth and yttrium compounds have previously been described[12].

All other reagents were of C.p. quality.

Thermobalance. The thermobalance used has been previously described[12]. The weight of the samples ranged from 100 to 150 mg.

The heating rates on all the samples were 4.5° per minute with a maximum temperature limit of about 900°C. Duplicate and in some cases triplicate samples were run on each chelate with a resulting agreement to each other within 1%.

Preparation of the chelates. About 0.1 g of the rare earth metal chloride hydrate was dissolved in 50 ml of water. To this solution were added 10 ml of a 2*M* ammonium acetate solution and a sufficient amount of the reagent to completely precipitate the metal ions. The reagent solutions consisted of the following: DCQ, 1% (W/V) in acetone; DBQ, 0.5% (W/V) in acetone; DIQ, 0.5% (W/V) in dioxane. Immediately upon adding the reagent, yellow color precipitates were obtained. However, with cerium, the precipitates turned purple on standing. In all cases, the best results were obtained by precipitating the chelates at room temperature. Basic salts were formed at higher precipitation temperatures (80-90°C). The resulting precipitates were allowed to stand at room temperature for 3 to 4 hours, filtered into sintered porcelain crucibles, washed three times with water and then air dried for 24 hours at room temperature.

DISCUSSION

The thermal decomposition curve of each of the rare earth chelates will be discussed individually with a correlation of results at the end of the discussion.

Lanthanum chelates. The thermal decomposition curves of the lanthanum chelates are shown in Fig. 1. The lanthanum DCQ chelate, $La(C_9H_4Cl_2NO)_3$, began to lose weight at 95°C.

The rate of decomposition increased rapidly above 210°C to give the La_2O_3 level at 780°C. The lanthanum DBQ chelate, $La(C_9H_4Br_2NO)_3$, was slightly more stable in that the first weight loss occurred at 125°C. Above 340°C the rate of decomposition increased rapidly to give the La_2O_3 level at 740°C. The thermal decomposition of the lanthanum DIQ chelate, $La(C_9H_4I_2NO)_3$, has previously been discussed[11].

Cerium chelates. The reaction of cerium (III) salts with the 5,7-dihalo-8-quinolinols proved unusual in that an oxidation occurred during the precipitation to give chelates containing tetravalent cerium. It was found that on introduction of the reagent to a solution of a cerium (III) salt, a yellow-brown colored precipitate first formed which on standing for 3 to 4 hours, turned a dark purple color. Apparently, air oxidation converted the Ce (III) to Ce (IV). The general formula for the dark purple chelates corresponded to $Ce(C_9H_4X_2NO)_4$; where X is chlorine, bromine or iodine.

The thermal decomposition curves for the cerium chelates are shown in Figs. 1 and 2. The chelate stability and the minimum oxide level temperatures corresponded to the sequence, listed in order of decreasing temperature: DCQ > DBQ > DIQ. The cerium DCQ chelate, $Ce(C_9H_4Cl_2NO)_4$, began to lose weight at 105° C. Beyond this temperature there was little weight loss until 305°C. After a period of rapid decomposition, the CeO_2 level was obtained at 575°C. As in previous studies, the oxide level temperatures of the cerium chelates were much lower than the other rare earth metal chelates.

The cerium DBQ chelate, $Ce(C_9H_4Br_2NO)_4$, began to lose weight at 90°C. Beyond 390°C the rate of decomposition increased rapidly resulting in the CeO_2 level at 520°C. The cerium DIQ chelate, $Ce(C_9H_4I_2NO)_4$, began to lose weight at 85°C. Above this temperature the decomposition proceeded rapidly to give the CeO_2 level at 385°C.

Praseodymium chelates. The thermal decomposition curves of the praseodymium chelates are shown in Fig. 2. The praseodymium DCQ chelate, $Pr(C_9H_4Cl_2NO)_3$, began to lose weight at 85°C. Aboven 190°C the rate of decomposition increased rapidly, resulting in a horizontal from 255° to 310°C.

The composition of this horizontal did not correspond to any stoichiometric compound and was probably a mixture of decomposition products. Further decomposition took place above 310°C resulting in the Pr_6O_{11} level at 690°C. The praseodymium DBQ chelate, $Pr(C_9H_4Br_2NO)_3$, exhibited the greatest thermal stability of all of the praseodymium chelates. The first weight loss occurred at 105°C with the rate of decomposition increasing rapidly above 400°C to give the Pr_6O_{11} level at 755°C. The praseodymium DIQ chelate, $Pr(C_9H_4I_2NO)_3$, began to lose weight at 85°C, with decomposition proceeding continuously beyond this point to give the Pr_6O_{11} level at 520°C.

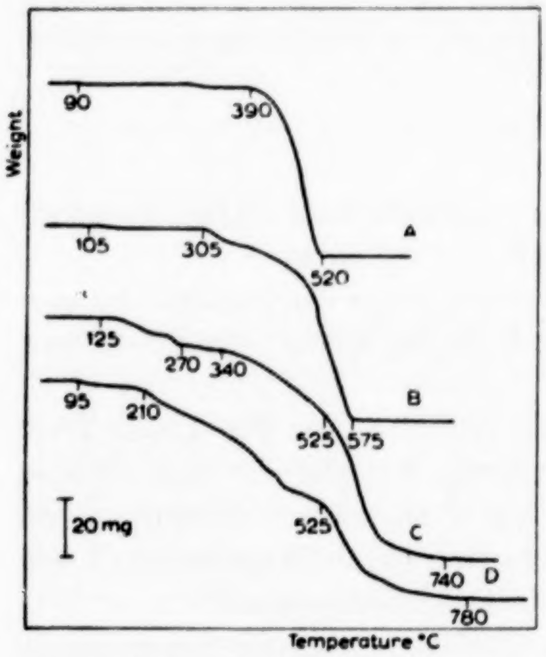

Fig. 1. Thermal decomposition curves of the rare earth metal chelates.
A. Cerium (IV) 5,7-dibromo-8-quinolinol chelate.
B. Cerium (IV) 5,7-dichloro-8-quinolinol chelate.
C. Lanthanum 5,7-dibromo-8-quinolinol chelate.
D. Lanthanum 5,7-dichloro-8-quinolinol chelate.

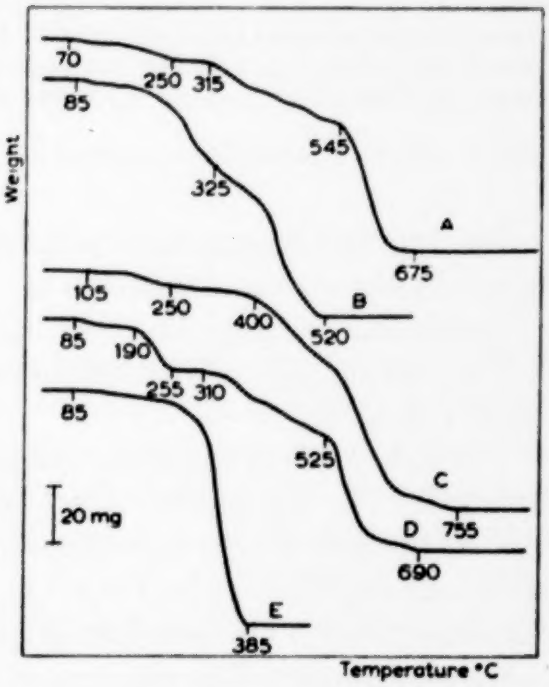

Fig. 2. Thermal decomposition curves of the rare earth metal chelates.
A. Neodymium 5,7-dichloro-8-quinolinol chelate.
B. Praseodymium 5,7-diiodo-8-quinolinol chelate.
C. Praseodymium 5,7-dibromo-8-quinolinol chelate.
D. Praseodymium 5,7-dichloro-8-quinolinol chelate.
E. Cerium (IV) 5,7-diiodo-8-quinolinol chelate.

Neodymium chelates. The thermal decomposition curves of the neodymium chelates are shown in Figs. 2 and 3. The neodymium DCQ chelate, $Nd(C_9H_4Cl_2NO)_3$, began to lose weight at 70°C. Above 315°C the rate of decomposition increased rapidly to give the Nd_2O_3 level at 675°C. The neodymium DBQ chelate, $Nd(C_9H_4Br_2NO)_3$, exhibited the least thermal stability of all of the neodymium chelates. The first weight loss occurred at 65°C, with the rate of decomposition increasing rapidly beyond 365°C to give the Nd_2O_3 level at 730°C. The neodymium DIQ chelate, $Nd(C_9H_4I_2NO)_3$, began to lose weight at 90°C. Above 225°C the rate of decomposition increased rapidly resulting in the Nd_2O_3 level at 350°C.

Samarium chelates. The thermal decomposition curves of the samarium chelates are shown in Fig. 3. The samarium DCQ chelate, $Sm(C_9H_4Cl_2NO)_3$, began to lose weight at 80°C. Beyond this initial weight loss, two horizontals were found in the curve. The first was from 115 to 180°C, with the second extending from 250 to 300°C. Neither horizontal corresponded to any stoichiometric compound and were probably mixtures of decomposition products. Above 300°C the rate of decomposition increased rapidly to give the Sm_2O_3 level at 645°C. The samarium DBQ chelate, $Sm(C_9H_4Br_2NO)_3$, was the least stable thermally. After the first weight loss at 75°C the rate of decomposition proceeded slowly up to 365°C, then increasing rapidly above this temperature to give the Sm_2O_3 level at 795°C. The samarium DIQ chelate, $Sm(C_9H_4I_2NO)_3$, began to lose weight at 90°C. Above 200°C the rate of decomposition increased rapidly to give the Sm_2O_3 level at 585°C.

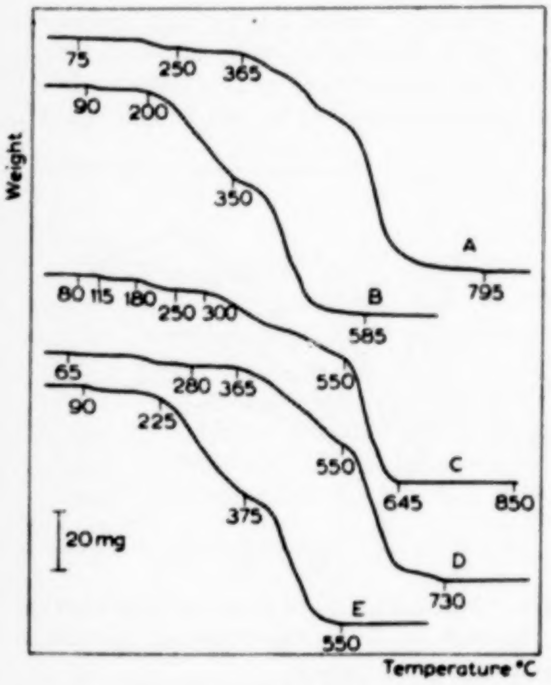

Fig. 3. Thermal decomposition curves of the rare earth metal chelates.
A. Samarium 5,7-dibromo-8-quinolinol chelate.
B. Samarium 5,7-diiodo-8-quinolinol chelate.
C. Samarium 5,7 dichloro-8-quinolinol chelate.
D. Neodymium 5,7-dibromo-8-quinolinol chelate.
E. Neodymium 5,7-diiodo-8-quinolinol chelate.

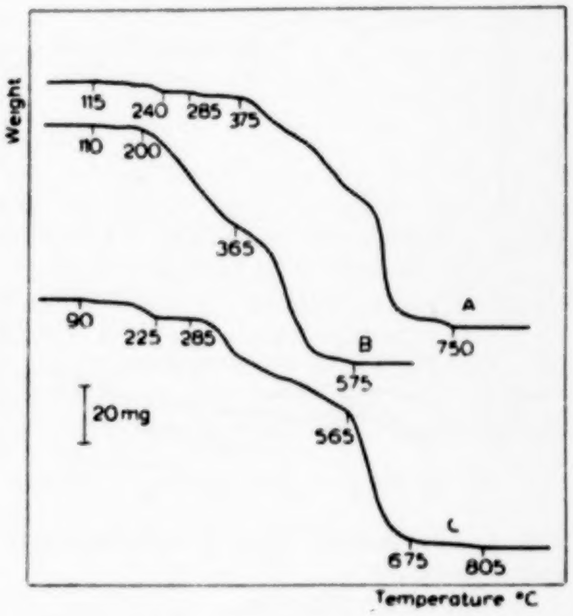

Fig. 4. Thermal decomposition curves of the yttrium chelates.
A. Yttrium 5,7-dibromo-8-quinolinol chelate.
B. Yttrium 5,7-diiodo-8-quinolinol chelate.
C. Yttrium 5,7-dichloro-8-quinolinol chelate.

Yttrium chelates. The thermal decomposition curves of the yttrium chelates are shown in Fig. 4. The yttrium DCQ chelate, $Y(C_9H_4Cl_2NO)_3$, began to lose weight at 90°C. From 225 to 285°C a horizontal level was found but the composition did not correspond to any stoichiometric formula. Beyond 285°C the rate of decomposition increased rapidly to give a mixture containing carbonaceous matter at 675°C. This was gradually oxidized to give the Y_2O_3 level at 805°C. The yttrium DBQ chelate, $Y(C_9H_4Br_2NO)_3$, was the most stable of all of the yttrium chelates. The first weight loss was observed at 115°C. After various stages of slow decomposition, the rate of decomposition increased rapidly beyond 375°C to give the Y_2O_3 level at 750°C. The yttrium DIQ chelate, $Y(C_9H_4I_2NO)_3$, began to lose weight at 110°C. After the initial loss in weight, little decomposition took place until after 200°C. The rate of decomposition then increased rapidly to give the Y_2O_3 level at 575°C.

General observations on the rare earth chelates. Using the data presented in this paper and from previous papers[8,10,11,13], interesting temperature stability relationships can be seen in the curves in Figs. 5 and 6. Fig. 5 shows the variation of the chelate stability temperature with atomic number of the metal ion. These curves show the following general sequence, in order of decreasing thermal stability: 8-quinolinol $\gg$ DCQ $>$ DIQ $>$ DBQ $>$ 2-methyl-8-quinolinol. Thus, it can be seen that substitution of halogen atoms on the 5,7-position or a methyl group on the 2-position of the 8-quinolinol molecule, tends to lower the decomposition temperature of the metal chelate. Concerning the thermal stability of the chelates with the same chelating agent, the trend seems to be, in decreasing order of stability La $>$ Ce $>$ Pr $>$ Nd $>$ Sm $>$ Y. This appears to hold in all cases except for the DBQ and DIQ chelates where there was a slight increase in stability in going from Sm to Y.

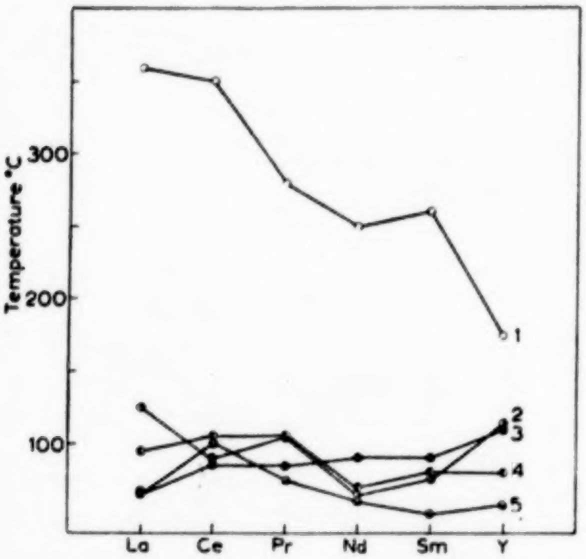

Fig. 5. Thermal stability of the rare earth metal chelates.
1. 8-Quinolinol chelates.
2. 5,7-Dibromo-8-quinolinol chelates.
3. 5,7-Diiodo-8-quinolinol chelates.
4. 5,7-Dichloro-8-quinolinol chelates.
5. 2-Methyl-8-quinolinol chelates.

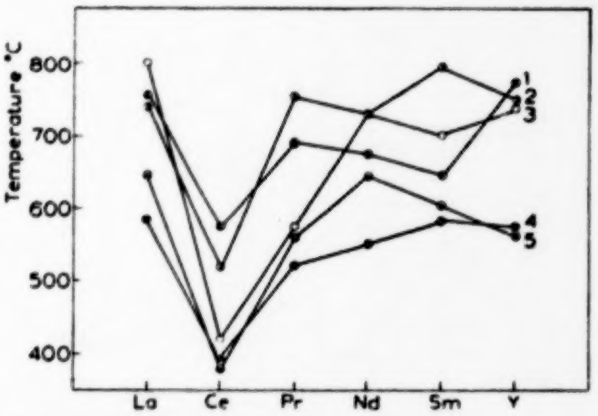

Fig. 6. Minimum oxide level temperatures for the rare earth metal chelates. Heating rate 4.5°C per minute.
1. 5,7-Dichloro-8-quinolinol chelates.
2. 5,7-Dibromo-8-quinolinol chelates.
3. 8-Quinolinol chelates.
4. 5,7-Diiodo-8-quinolinol chelates.
5. 2-Methyl-8-quinolinol chelates.

The minimum oxide level temperatures for the metal chelates are shown in Fig. 6. An outstanding observation from this plot is the minimum in the curves at cerium. The CeO_2 levels were obtained from 200 to 400°C lower than the La_2O_3 levels. The oxide level temperatures for the chelates, listed in order of decreasing temperature are roughly: DBQ $>$ 8-quinolinol $>$ DCQ $>$ 2-methyl-8-quinolinol $>$ DIQ. For a given chelating agent, lanthanum had the highest oxide level temperature which, after the minimum at cerium, gradually decreased in magnitude with the other rare earth elements.

SUMMARY

The thermal decomposition of the 5,7-dichloro-, 5,7-dibromo- and 5,7-diiodo-8-quinolinol chelates of lanthanum, cerium, praseodymium, neodymium, samarium and yttrium was investigated on the thermobalance. The chelates decomposed in the temperature range from 65 to 125°C while the oxide levels were obtained from 395 to 805°C. Although the chelate thermal stability tempera-

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tures varied little with the chelating agent, the minimum oxide level temperatures were largely dependent on the halogen substitution on the 8-quinolinol molecule. Results of this study were correlated with previous studies on the rare earth metal chelates with 8-quinolinol and 2-methyl-8-quinolinol.

RÉSUMÉ

La décomposition thermique des 5,7-dichloro-, 5,7-dibromo- et 5,7-diiodo-8-quinolinol chélates de lanthane, cérium, praséodyme, néodyme, samarium et yttrium est étudiée sur la thermobalance. Les chélates se décomposent à des températures de l'ordre de 65 à 125°C tandis que le niveau des oxydes est obtenu de 395 à 805°C. Quoique les températures de stabilité thermale des chélates varient peu avec l'agent ,,chélatant'', les températures niveau minimales des oxydes dépendent grandement de la substitution de l'halogène dans la molécule de 8-quinolinol.

Les résultats de cette étude sont mis en corrélation avec des études précédentes sur les chélates métalliques des terres rares avec le 8-quinolinol et le 2-méthyl-8-quinolinol.

ZUSAMMENFASSUNG

Die Thermolyse der 5,7-Dichloro-, 5,7-Dibromo- und 5,7-Dijodo-8-oxychinolin-Chelate von Lanthan, Cer, Praseodym, Neodym, Samarium und Yttrium wurde auf der Thermowaage untersucht. Die Chelate zersetzten sich in dem Temperaturbereich von 65 bis 125°C während die Oxydstufen zwischen 395 und 805°C erreicht wurden. Während sich die Temperaturen bei denen die Chelate beständig sind, nur wenig mit dem chelatbildenden Reagenz änderten, waren die Minimaltemperaturen der Oxydstufe weitgehend von der Halogensubstitution in dem 8-Oxychinolinmolekül abhängig. Die Ergebnisse dieser Untersuchung wurden met früheren Arbeiten über die Chelate der seltenen Erden mit 8-Oxychinolin und 2-Methyl-8-oxychinolin in Zusammenhang gebracht.

REFERENCES

[1] R. Berg and E. Becker, *Z. anal. Chem.*, 119 (1940) 1.

[2] N. Eswaranarayana and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, 11 (1954) 339.

[3] G. Mannelli, *Atti congr. intern. chim., 10th Congr., Rome, 1938 (publ. 1939)*, 2 (1938) 718.

[4] S. Misumi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 73 (1952) 931.

[5] S. Misumi, *ibid.*, 74 (1953) 453.

[6] T. Moeller and D. E. Jackson, *Anal. Chem.*, 22 (1950) 1393.

[7] T. I. Pirtea, *Z. anal. Chem.*, 107 (1936) 191; *Bull. chim. soc. roumaine chim.*, 39 (1937-38) 83.

[8] W. W. Wendlandt, *Anal. Chim. Acta*, 15 (1956) 109.

[9] W. W. Wendlandt, *Science*, 124 (1956) 682.

[10] W. W. Wendlandt, *Anal. Chim. Acta*, in the press.

[11] W. W. Wendlandt, *ibid.*, 15 (1956) 533.

[12] W. W. Wendlandt, *Anal. Chem.*, 27 (1955) 1277.

[13] W. W. Wendlandt, *ibid.*, 28 (1956) 499.

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STUDIES IN POLAROGRAPHIC ANALYSIS

I. DETERMINATION OF MANGANESE AFTER OXIDATION TO THE MANGANIC STATE STABILIZED BY TRIETHANOLAMINE

by

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In the polarographic determination of manganese two types of procedures are involved. In the first procedure, manganous solutions are directly electrolysed in the presence of a suitable supporting electrolyte[1].

In the second[2], Mn^{+2} is oxidised by lead dioxide in the presence of pyrophosphate and, after filtering off the excess oxidant, the filtrate containing the manganic pyrophosphate complex is polarographed.

MOJŽIŠ[3] also took advantage of the tendency of Mn^{+2} to be oxidized to Mn^{+3} by atmospheric oxygen in alkaline solutions containing triethanolamine in order to determine manganese, especially in the presence of iron, nickel, and lead. Similarly, NOVAK, KUTA AND RIHA[4] and in a later investigation RIHA AND SERÀK[5] studied the polarography of Mn^{+3} and Fe^{+3} in the same supporting electrolyte and concluded that the oxidation of Mn^{+2} to Mn^{+3} is associated with peroxide formation.

In this investigation, the work of the above-mentioned authors is extended with the view of obtaining other characteristics of the manganic wave.

EXPERIMENTAL

Preparation of solutions

A. Manganous solutions. 0.0988*M* Mn^{+2} was prepared by dissolving manganous sulphate in 0.1*M* H_2SO_4. The manganese content was estimated by the Mn^{+4}-tellurate method[6]. From this solution others of lower concentration were prepared by appropriate dilution.

B. Triethanolamine solution. A solution, 50% triethanolamine by volume, was prepared by dilution of one part commercial grade product with tierce parts distilled water.

C. Sodium hydroxide solution. 5*M* NaOH solution was prepared from the AnalaR product.

Analytical procedure

0.5-2.5 ml of the 0.00988 or 0.0988*M* Mn^{+2} solution is placed in a 25 ml measuring flask together with sufficient triethanolamine to make the final solution 4% amine by volume. After adding enough alkali to make the solution 0.5*M*, the mixture is made up to 25 ml and mixed thoroughly. The resulting solution is placed in a dry conical flask and a current of air is allowed to bubble through it for a length of time proportional to the concentration of the Mn^{+2} present. The time of bubbling necessary for complete oxidation was deduced from a comparison of the diffusion current observed after different intervals with solutions prepared under conditions which ensure complete oxidation of Mn^{+2} to Mn^{+3} (60 min at a rate of 120 bubbles per min). The time necessary for this procedure was found to be 5 and 10 minutes in 1 m*M* and 5 m*M* solutions, respectively. When a 10 m*M* solution was used, a brown precipitate was observed and the diffusion current was lower than corresponded to the amount of manganese present.

The same results were obtained when air was bubbled through the mixture, placed in the measuring flask, and made up to the mark.

To study the effect of concentrations of alkali or triethanolamine, the necessary amounts were mixed with the manganese solution to give 0.2-3*M* of the former and 2-10% of the latter.

After the solution was prepared in this manner, it was placed in the polarographic cell; pure hydrogen or nitrogen was bubbled through for 15 min, after which the solution was polarographed. Sodium sulphite was also tested as a means of removing dissolved oxygen, and N_2 was bubbled through it for only 2 min.

The capillaries used had the following characteristics:

(a) $m_1 = 3.26$ mg/sec and $t_1 = 2.31$ sec.
(b) $m_2 = 3.13$ mg/sec and $t_2 = 2.07$ sec.

Unless otherwise stated, the measurements were carried out at 25°C.

The cell used in these measurements was the same as previously described[8]. For recording the polarograms an ink recording polarograph of the Radiometer type was used.

RESULTS

The polarograms obtained by the reduction of manganic-triethanolamine complex, drawn by taking the middle of the oscillation to represent the diffusion current, are represented in Figs. 1 and 2.

In Fig. 1 complete polarograms are shown, each consisting of two waves. The first wave represents the reduction of the Mn^{+3} to the bivalent state and starts at —0.4 V *vs.* S.C.E. The second wave represents the reduction of Mn^{+2} to metallic manganese and starts at —1.6 V. The first wave is well developed while the second is not and possesses a smaller diffusion current that is apparently due to the partial precipitation of manganous hydroxide before its reduction to metallic manganese. This is confirmed by the fact that on electrolysing alkaline manganous solutions containing triethanolamine, the diffusion current of both anodic and cathodic waves does not vary linearly

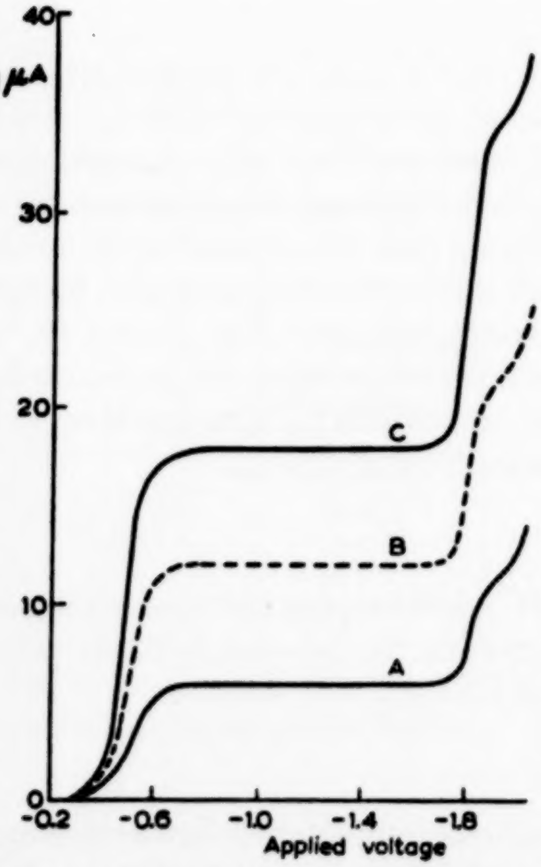

Fig. 1. Polarograms of the manganic triethanolamine complex in 0.5*M* NaOH + 4% triethanolamine. Oxidised by H_2O_2. A: 2 m*M* Mn; B: 4 m*M* Mn; C: 6 m*M* Mn.

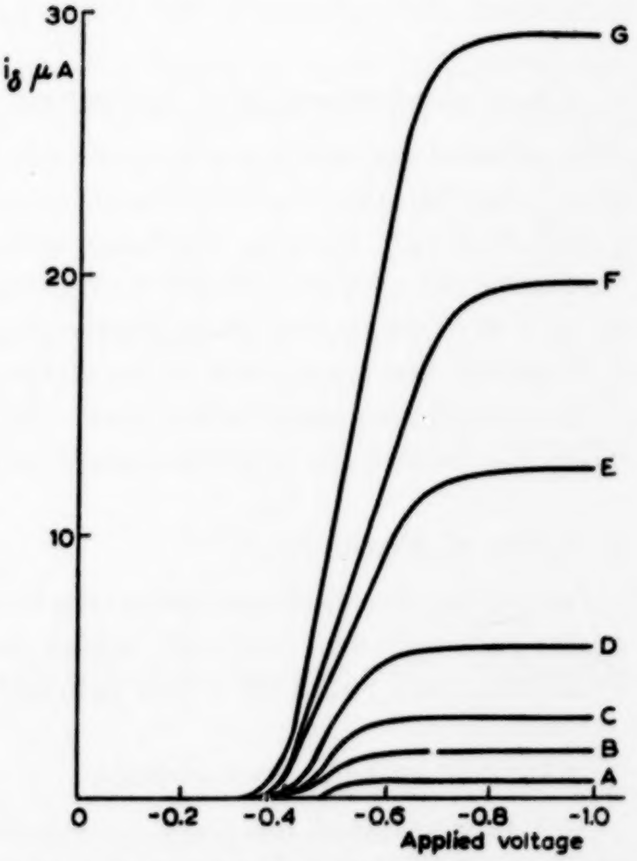

Fig. 2. Polarograms of the manganic triethanolamine complex in 0.5*M* NaOH + 4% triethanolamine. A: 0.2 m*M* Mn; B: 0.57 m*M* Mn; C: 1.0 m*M* Mn: D: 2.0 m*M* Mn; E: 4.17 m*M* Mn; F: 6.67 m*M* Mn.

with the concentration of manganese. It was further observed that precipitation occurs when the concentration of Mn^{+2} exceeds 2 mM.

We therefore limited our study in the analysis of manganese to the first wave involving the reduction of the manganic complex to the manganous state. The present study includes the effect of temperature and alkalinity, together with the concentrations of triethanolamine, sodium sulphite, and manganese, on the diffusion current.

At first, a solution of the triethanolamine complex was prepared by the method of GIBAUD[7], *i.e.* by bubbling air through a mixture of equal volumes of triethanolamine and $2.5M$ NaOH mixed with 10 ml of $0.0988M$ Mn^{+2} solution for 24 hours to ensure complete oxidation. The mixture was made up to 100 ml so that the concentration of Mn^{+2} was $0.00988M$. From this solution, successive portions were added from a small burette (at 18°C) to 10 ml of $0.5M$ NaOH, which had been freed from oxygen by a stream of pure nitrogen to yield solutions $2\cdot10^{-4}$ to $5\cdot10^{-3}M$. The nitrogen stream was passed through the solution for 2 minutes after each addition. Alternately, 10 ml of the $0.00988M$ Mn^{+3} solution were freed from dissolved oxygen and successive portions of $0.5M$ alkali were added to give solutions of concentration ranging from $9.9\cdot10^{-3}$—$5\cdot10^{-3}M$.

The curves shown in Fig. 2 indicate that the diffusion current obtained under these conditions is well developed and varies linearly with the concentration of manganese within the range $2\cdot10^{-4}$—$9.9\cdot10^{-3}M$ (*cf.* curve A Fig. 3).

In the following set of experiments the tervalent complex was developed by oxidizing separate portions of the manganous solution, after mixing them with the other reagents and making the solution up to the appropriate volume. The different factors previously mentioned were studied in the following order:

1. Effect of triethanolamine concentration

At alkali concentration as low as $0.2M$ NaOH it was found that with 2% triethanolamine the diffusion current varies linearly with the manganese concentration up to 4 mM. With 4% to 10%, the range of concentration could be extended up to 5 mM. On raising the alkalinity of the medium to $0.5M$ the diffusion current increases linearly up to 7 mM manganese even in presence of 4% triethanolamine (Fig. 3 curve B).

However, the magnitude of the diffusion current decreases when the concentration of the complexing agent is increased. The decrease amounts to 1 μA for a mM solution when the percentage of triethanolamine is increased from 4 to 10%.

2. Effect of alkalinity

Increasing the alkali concentration from 0.2-$3M$, while keeping the % of triethanolamine concentration constant, brings about a considerable decrease in the i_d values amounting to 1.76 μA for 2 mM solution and 0.92 μA for 1 mM solution.

3. Effect of sulphite concentration

As has been stated, it is possible to decrease the time of bubbling nitrogen or hydrogen through the solution in the presence of sodium sulphite to $\sim$ 2 min instead of 15 minutes. However, the results obtained in the presence of different concentrations of sulphite indicate that the wave height decreases in presence of sulphite and that the decrease is proportional to the amount of sulphite added. The data shown in Table I

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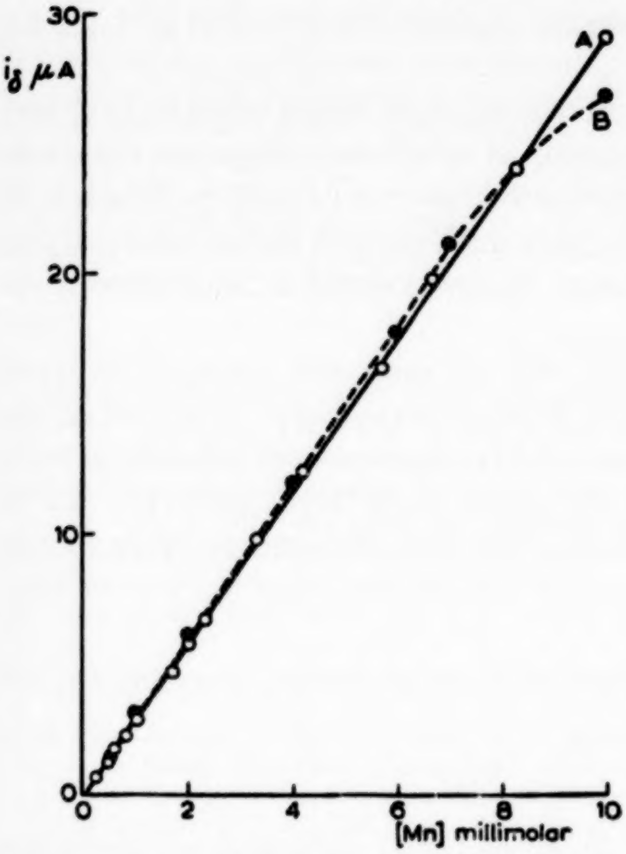

Fig. 3. Relation between i_d and Mn in 0.5 M NaOH + 4% triethanolamine. A: prepared stock by Gibaud's method; B: samples oxidised separately by H_2O_2.

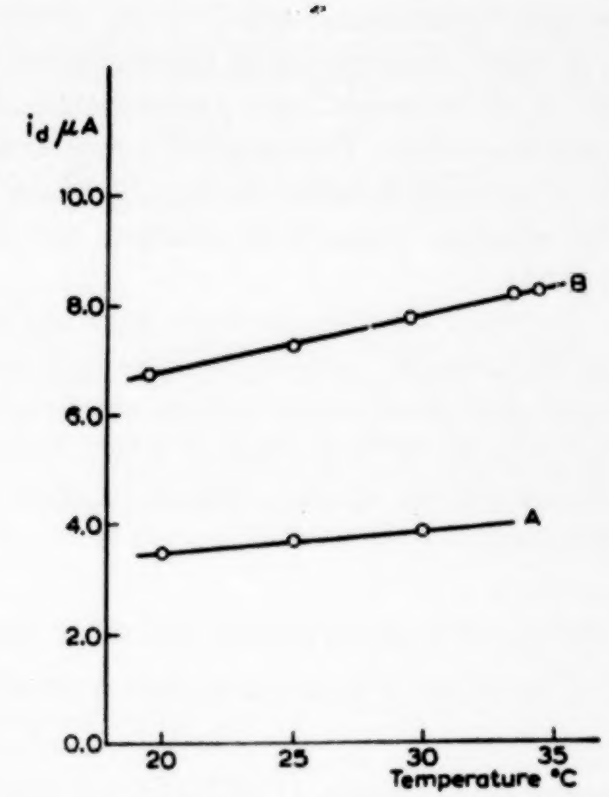

Fig. 4. Effect of temperature on the i_d of Mn in 0.5M NaOH + 4% triethanolamine. A: 1 mM Mn; B: 2 mM Mn.

indicates that for the same weight of sulphite added, the percentage decrease in diffusion current is approximately the same for two different concentration of manganese. This explains why one still obtains linear variation of the diffusion current with concentration in the presence of sulphite.

TABLE I

% DECREASE IN DIFFUSION CURRENT

Wt. of sulphite g	*1 mM Mn*	*8 mM Mn*
0.1	2.78	1.79
0.2	6.40	5.95
0.5	9.50	9.00
0.7	12.10	11.30

However, it is safer to remove dissolved oxygen without the use sulphite unless the necessary accuracy is not high.

4. *Effect of temperature*

Rise in temperature increases the value of i_d. The curves in Fig. 4 show that the temperature coefficient amounts to 1.2% per °C, a value which is of the same order of magnitude as that given by MEITES[9].

From the above results, it is apparent that the optimum conditions for the polarographic determination of manganese is to make the medium 0.5M NaOH and 4% by volume triethanolamine.

Under these conditions, the maximum amount of manganese which could be analysed is 7 mM. In case of higher concentrations, a portion of manganese separates out as an insoluble oxide. The range of concentration can be increased to 8 mM in presence of 10% triethanolamine. On the other hand, when hydrogen peroxide is used for oxidizing the alkaline manganous solution, the manganese analysed could be increased up to 10 mM.

Excess hydrogen peroxide does not interfere with the manganic-manganous wave as its diffusion current becomes well developed before the reduction potential of the hydrogen peroxide. It will do so with ferric iron wave, if present in admixture with manganese (to be published later). However, the effect of hydrogen peroxide can be eliminated by adding sodium sulphite which removes all hydrogen peroxide in few minutes.

VALUES OF THE DIFFUSION CURRENT CONSTANT I AND THE DIFFUSION COEFFICIENT D°

The values of I, as calculated from the relation

$$I = i_d/m^{2/3}\, t^{1/6} = 607\, n\, D^{\circ 1/2}$$

are shown in Table II. From these data it is apparent that I decreases by increasing both the alkali and the triethanolamine concentrations. However, under the optimum conditions chosen, (*i.e.*), in the presence of 4% triethanolamine and 0.5M NaOH, the value of I amounts to 1.27.

The value of D°, the diffusion coefficient, also decreases by increasing both the % of the triethanolamine and the alkali concentration. Under the conditions already chosen, $D^{\circ} = 4.18 \cdot 10^{-6}$ cm²/sec. Analysis of the wave by the use of the equation

$$E = E_{1/2} + RT/nF \ln i/i_d - i$$

gives a linear relation between E and $\ln i/i_d - i$. The slope amounting to 0.065 V does not differ much from the theoretical slope of 0.059 for a value of $n = 1$.

TABLE II

Triethanolamine by volume %	*Concentration of alkali* M	I	$D^{\circ} \cdot 10^{6}$
2	0.2	1.40	5.32
4	0.2	1.31-1.33	4.35
10	0.2	1.20	3.91
4	0.5	1.27	4.18
4	1.0	1.20	3.91
4	2.00	1.12	3.69
4	3.0	0.96	3.00

SUMMARY

The manganic complex with triethanolamine, prepared by the oxidation of manganous solution in presence of 0.5M NaOH and 4% by volume triethanolamine with atmospheric oxygen, is found suitable for the polarographic determination of manganese. Under these conditions, the diffusion current is proportional to the Mn^{+2} concentration from 2.10^{-4}-$7.10^{-3}M$. $E_{1/2}$ for the Mn^{+3}/Mn^{+2} wave $= -0.5$ V *vs.* S.C.E. The temperature coefficient for the diffusion current is 1.2% per degree. I and D° decrease by increasing the alkali or triethanolamine concentration. They amount in presence of NaOH $= 0.5M$ and 4% triethanolamine to $I = 1.27$ and $D^{\circ} = 4.18 \cdot 10^{-6}$ cm²/sec.

RÉSUMÉ

Le complexe manganèse(III)-triéthanolamine, obtenu par oxidation du manganèse(II) par l'oxygène de l'air, en présence d'hydroxyde de sodium 0.5M et de triéthanolamine à 4%, peut être utilisé pour le dosage polarographique du manganèse. Dans les conditions observées, le courant de diffusion varie linéairement pour des concentrations en manganèse allant de 2.10^{-4} à $7.10^{-3}M$. La valeur $E_{1/2}$ est égale à —0.5 V (*vs.* E.C.S.). Le coefficient de température du courant de diffusion est de 1.2% par degré. Les valeurs de I et D° diminuent en fonction de l'augmentation des concentrations en hydroxyde alcalin et en triéthanolamine. En présence de NaOH 0.5M et de 4% de triéthanolamine, $I = 1.27$ et $D^\circ = 4.18 \cdot 10^{-6}$ cm²/sec.

ZUSAMMENFASSUNG

Der Mangan(III)komplex mit Triäthanolamin der durch Oxydation einer Mangan(II)lösung in Anwesenheit von 0.5M NaOH und 4 Volumprozent Triäthanolamin mit Luftsauerstoff hergestellt wird, hat sich für die polarographische Bestimmung des Mangans gut bewährt. Der Diffusionstrom ist der Mangankonzentration von 2.10^{-4} bis $7.10^{-3}M$ proportional. Für die Welle Mn^{+3}/Mn^{+2} ist $E_{1/2}$ = —0.5 V gegen die gesättigte Kalomelektrode. Der Temperaturkoeffizient für den Diffusionstrom ist 1.2% pro Grad. I und D nehmen ab wenn die Alkali- und die Triäthanolaminkonzentration zunehmen. Sie betragen in Anwesenheit von 0.5M NaOH und 4% Triäthanolamin $I = 1.27$ und $D^\circ = 4.18 \cdot 10^{-6}$ cm²/sec.

REFERENCES

[1] E. Hamamoto, *Collection Czechoslov, Chem. Communs.*, 6 (1938) 315.
J. Prajsler, *Collection Czechoslov, Chem. Communs.*, 3 (1931) 406.
M. Voriskva, *Collection Czechoslov, Chem. Communs.*, 11 (1939) 588.
E. T. Verdier, *Collection Czechoslov, Chem. Communs.*, 11 (1939) 216.
E. T. Verdier, *Collection Czechoslov, Chem. Communs.*, 11 (1939) 233.

[2] I. M. Kolthoff and J. I. Watters, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 8.

[3] J. Mojžiš, *Proc. Intern. Polarogr. Congress, Prague*, 1951, Pt. I (1951) 638, Pt. III (1952) 464.

[4] J. V. A. Novak, J. Kuta and J. Riha, *Chem. listy*, 47 (1953) 649.

[5] J. Riha and L. Seràk, *Collection Czechoslov, Chem. Communs.*, 20 (1955) 640.

[6] I. M. Issa and I. F. Hewaidy, *Chemist Analyst*, 55 (1955) 70.

[7] M. Gibaud, *Compt. rend.*, 236 (1953) 814.

[8] I. M. Issa, S. E. Khalafalla and R. M. Issa, *Rec. trav. chim.*, 75 (1956) 1031.

[9] L. Meites, *Polarographic Techniques*, Interscience Publishers, London, 1956, p. 56.

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RESOLUTION OF CRYSTALLINE RIBONUCLEASE BY PAPER ELECTROPHORESIS

by

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INTRODUCTION

Modifications and refinements in the techniques of paper electrophoresis may increase the efficacy of this technique for fractionating proteins beyond its present value. The present report is an elaboration of effects on the resolution of ribonuclease fractions on paper produced by two-dimensional electrophoresis. The aim of this procedure is to provide a more accurate analytical standard of enzyme purity by demonstrating possible heterogeneity of crystalline enzyme, which was reported[1] to be homogeneous when it was studied in the Tiselius electrophoresis. Crystalline ribonuclease (RNase) has been shown to be resolvable into two components by partition[2], as well as by ion exchange resin[3] chromatography.

The present investigations with paper electrophoresis revealed for the first time the analytical resolution capacity of two-dimensional paper electrophoresis. Crystalline ribonuclease consisted of at least four enzymically active components resolvable by paper electrophoresis. The specific enzymic activity of each of the fractions is demonstrated.

EXPERIMENTAL

Materials

Cytidine-2′,3′-phosphate and adenosine-2′,3′-phosphate were synthesized chemically by the method of Brown, Magrath and Todd[4].

Guanosine-2′,3′-phosphate was isolated by a previously described procedure[5], as modified by Heppel, Whitfeld and Markham[6].

Uridine-2′,3′-phosphate was isolated from RNase digests of ribonucleic acid as described by Markham and Smith[5].

Ribonucleases were prepared in the laboratory in crystalline form from calf pancreas[7], or were obtained commercially from Armour and Co., Worthington Chemical Co., and Nutritional Biochemical Corp., as in an earlier investigation[8].

Yeast ribonucleic acid was prepared as reported[9] and described [10] previously.

Methods

Paper electrophoresis

Apparatus. Electrophoresis was accomplished in phosphate buffer (165.5 g of $NaH_2PO_4\cdot H_2O$ and 286.1 g of $Na_2HPO_4\cdot 12H_2O$, dissolved in 10 l distilled water, and pH adjusted to 6.49), using either (a) an electrophoretic apparatus or (b) the LKB 3276 electrophoresis equipment.

(a) The electrophoretic apparatus consist of a pair of 15″ square glass plates, between which a sheet of Whatman filter paper No. 1 was sandwiched. A 17″-square filter paper was prepared by cutting out a 2½″-square from each corner, so that a flap was provided on each side of the glass plates that were placed in the buffer reservoir containing platinum electrodes. After the paper was centered on the plate, polyethylene cover sheets were placed on the flap so that they extended about 25 mm om the paper, and then the top plate was added and clamped. Special care was taken to prevent inflow and air bubbles.

(b) In the LKB 3276 electrophoresis equipment 170 × 410 mm Whatman filter paper No. 3 MM was used. A 150 mm-square was cut out from the center of the paper, and a 152 mm-square of Whatman filter paper No. 3 MM was placed over the cut square.

Electrophoresis. In all experiments, ionic equilibration was accomplished in 24 hours. When using the two glass plates electrophoresis apparatus (a), a potential of 300 V, 0.5 mA current, was first applied in one direction for 24 hours at room temperature (approximately 18°C). The current was stopped, and under exactly the same conditions, a potential of 300 V, 0.5 mA current, was applied at right angles to the first current flow for an additional 24 hours. When using the LKB 3276 electrophoresis equipment, after ionic equilibration, a potential of 300 V, 0.5 mA current was applied for 24 hours. The current was stopped, the 152 mm-square of Whatman filter paper No. 3 MM was very carefully turned 90 degrees, and a potential of 300 V, 0.5 mA current was applied for an additional 24 hours.

Enzymic activity. From duplicate untreated electrograms triangular wedges were cut out of each of the four protein-containing sections. By dipping the broad side (tested for absence of proteins) of the paper in distilled water, the material was concentrated at the point of the wedge by capillary action and successive evaporation. After concentration, the pointed tip of each wedge was cut and placed in a small test tube (designed for microanalysis) to which was added 100 µml of 0.2*M* phosphate buffer, pH 7.2, containing 2 mg of yeast ribonucleic acid, and incubated at 37°C for 48 hours. Ten µml of chloroform were used as a bacteriostatic agent.

Enzymic activity on synthetic media was followed in a capillary tube, in which 100 µl of 1% solution of a cyclic anhydride in 0.1*M* acetate buffer (pH 6.5) was mixed with 10 µml of protein fraction I, II, III, or IV (obtained by dissolving the concentrated material at the pointed tip of each wedge as described in earlier section); this was incubated at 37°C for 3 hours, after sealing both ends of the capillary tube. One µl of chloroform was used to prevent bacterial growth. After incubation, the capillary tube was broken open and 2 µml were applied to Whatman filter paper No. 1 of a previously equilibrated electrophoresis apparatus. Controls consisted of cyclic nucleotide, exposed to similar experimental conditions in absence of enzyme fraction, and the nucleotide expected as end products. Electrophoresis of this section of investigation was performed in an electrophoresis apparatus as described by KUNKEL AND TISELIUS[11]. Sodium tetraborate, 0.4 M, pH 13, separated the cyclic anhydride and the nucleotide. A current of 10 mA at 1100 V, applied for one hour, resulted in a clear separation of the two groups. Separation of the 2'-isomer from the corresponding 3'-isomer of each of the mononucleotide was realized by the conditions described earlier[12].

Paper chromatography

Chromatograms of the digests of ribonucleic acid with each ribonuclease fractions (I, II, III, and IV) were developed by the descending technique in two dimensions. The solvent systems found to be of value were: solvent 1, ammonia-buffered-*iso*butyric acid as described by MAGASANIK *et al.*[13]; and solvent 2, *iso*propyl alcohol-acetic acid-water as described by MONTREUIL AND BOULANGER[14]. Permanent records of the chromatograms were obtained by the technique of MARKHAM AND SMITH[15]. After locating the mononucleotide areas, they were cut from the chromatograms. Complete elution was obtained by permitting 1 ml of distilled water to drain over the filter paper into a graduated centrifuge tube. Each eluant was adjusted finally to a vol. of 1.5 ml by the use of a dilute solution of HCl in such a proportion that the final concentration of HCl was 0.01 N. The ultraviolet absorption spectrum for each mononucleotide was determined by the use of a Beckman Model DU spectrophotometer and 1 ml capacity cells. Blanks were eluants of identical filter papers cut from blank chromatograms.

RESULTS

The resolution of crystalline ribonuclease into four enzymically active fractions is presented in Fig. 1. Electrophoresis in the first dimension produced no resolution; RNase moved as a homogeneous protein. The second-dimension electrophoresis resolved RNase into four enzymically active proteins.

Crystalline ribonucleases samples, prepared in the laboratory from calf pancreas, or obtained commercially from Armour and Co., Worthington Chemical Co., and Nutritional Biochemical Corp., when exposed to two-dimensional paper electrophoresis were resolved into the enzymically active fractions described in Table I. Only the sample obtained from Nutritional Biochemical Corp. was resolved into three components; all the other three samples were resolved into four components.

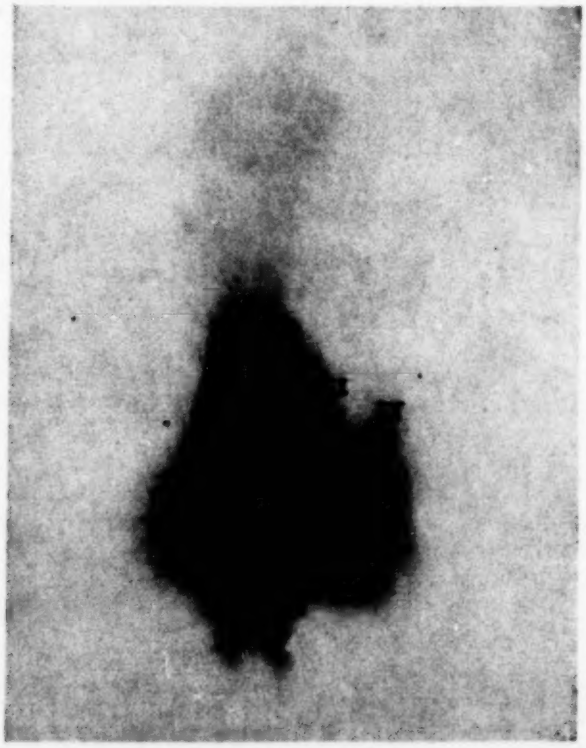

Fig. 1. Resolution of crystalline ribonuclease by two-dimensional paper electrophoresis ("detection reagent for protein-3").

TABLE I

RIBONUCLEASE ACTIVITY OF THE DIFFERENT ACTIVE FRACTIONS RESOLVED BY TWO-DIMENSIONAL PAPER ELECTROPHORESIS

	Original activity %	*Fractions resolved by paper electrophoresis*				*Recovery* %
		I	*II*	*III*	*IV*	
		% of original activity				
"Armour" Ribonuclease	100	48	41	6.5	2.5	98
"Worthington" Ribonuclease	100	49	43	3	2	97
"Nutritional Biochemicals" Ribonuclease	100	50	44	1	0	95
"Laboratory" Ribonuclease	100	49	41	6	1	97

Quantitative and qualitative differences are shown in the enzymic activity of the components of each sample.

Two-dimensional chromatographic analysis of the hydrolytic products resulting from enzyme action of the four components of RNase on yeast ribonucleic acid, using the solvent system ammonia-buffered-*iso*butyric acid, and *iso*propyl alcohol-acetic acid-water (Table II), revealed some interesting quantitative difference in mononucleotides liberated. Ribonuclease IV liberated more guanylic acid (10.5 moles/100 moles) than RNase III (2.5 moles/100 moles), RNase II (0.5 mole/100 moles), or RNase I (0.5 mole/100 moles). Ribonuclease III liberated more adenylic acid (8.5 moles/100 moles) than RNase IV (4.5 moles/100 moles), RNase II (2.5 moles/100 moles), or RNase I (0.5 moles/100 moles). Ribonuclease II liberated more cytidylic acid (18.5 moles/100 moles) than RNase I (17.4 moles/100 moles), RNase III (14.5 moles/100 moles) or RNase IV (10.5 moles/100 moles).

TABLE II

ACTION OF CRYSTALLINE RIBONUCLEASE FRACTIONS ON YEAST RIBONUCLEIC ACID

Fractions	*Mononucleotides liberated*			
	uridylic acid	*cytidylic acid*	*adenylic acid*	*guanylic acid*
	moles per 100 moles			
I	17.6	17.4	0.5	0.5
II	17.0	18.5	2.5	0.5
III	15.6	14.5	8.5	2.5
IV	11.5	10.5	4.5	10.5

Paper electrophoretic analysis of the hydrolytic products produced from enzyme action of each of the four ribonuclease components on the synthetic substrates, uridine-2′,3′-phosphate, cytidine-2′,3′-phosphate, adenosine-2′,3′-phosphate, or guanosine-2′,3′-phosphate (Table III), indicated that the major activity of RNase I was on uridine-2′,3′-phosphate, RNase II on cytidine-2′,3′-phosphate, RNase III on adenosine-2′,3′-phosphate, and RNase IV on guanosine-2′,3′-phosphate.

RNase (Armour) solution was kept at 0°C, and at period intervals, aliquots were assayed for enzyme activity and for two-dimensional paper electrophoresis. Enzymic activity was almost constant, diminished at most by approx. 2% after 66 days at 0°C. Paper electrophoresis revealed some quantitative difference in the ribonuclease components. RNase I and RNase II showed progressive decrease in activity, from 48

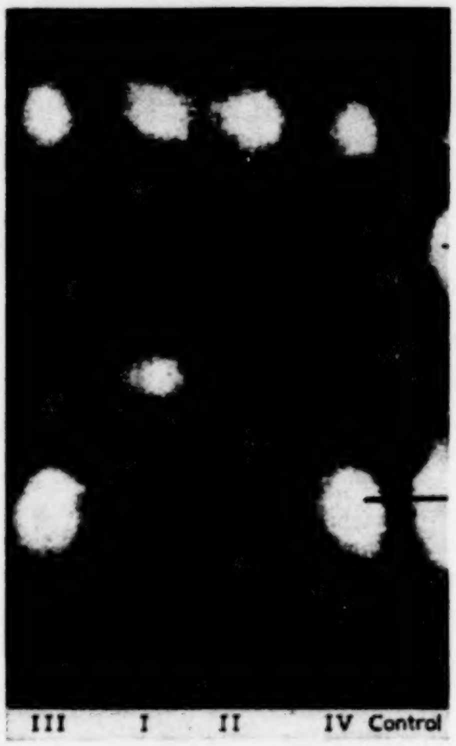
III
I
II
IV
Control

Fig. 2. Action of the four ribonuclease components on uridine-2',3'-phosphate.

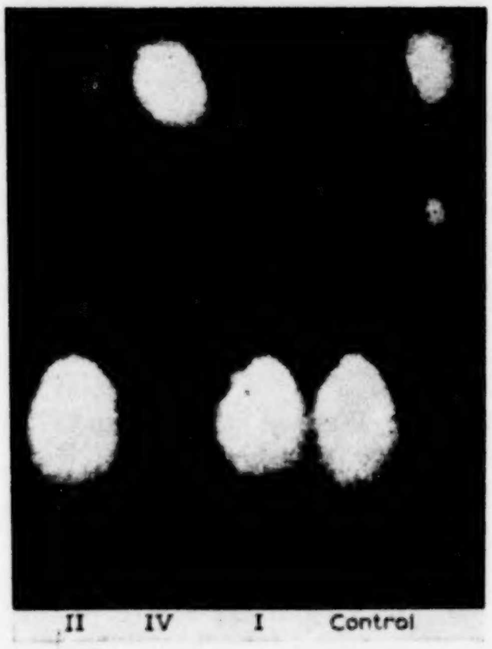
II
IV
I
Control

Fig. 3. Action of the four ribonuclease components on guanosine-2',3'-phosphate.

to 38, and from 41 to 37, respectively; RNase III and RNase IV activities progressively increased from 6.5 to 11, and from 2.5 to 9, respectively.

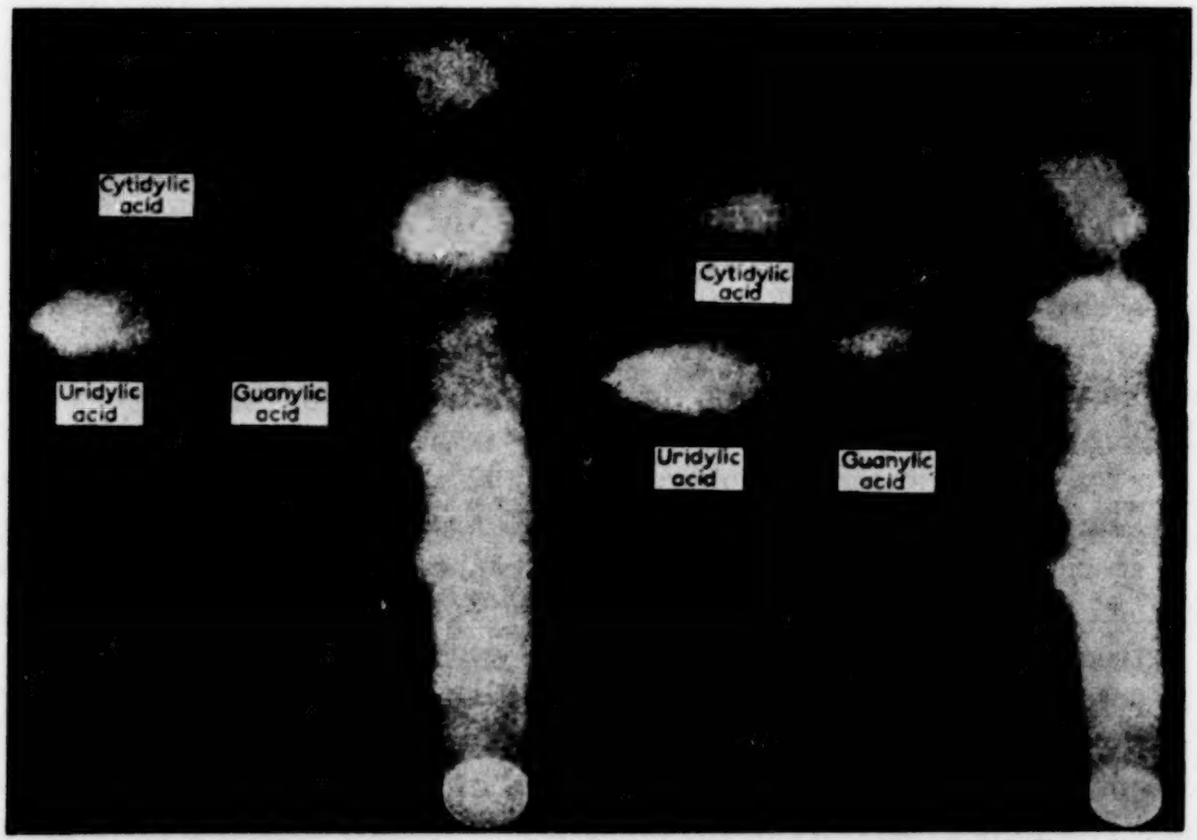
Cytidylic acid
Uridylic acid
Guanylic acid
Cytidylic acid
Uridylic acid
Guanylic acid

Fig. 4. Action of ribonuclease components I and IV on yeast ribonucleic acid. Two-dimensional chromatographic analysis of the hydrolytic products resulting from the action of ribonuclease components I and IV on yeast ribonucleic acid.

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TABLE III

ACTION OF CRYSTALLINE RIBONUCLEASE FRACTIONS ON SYNTHETIC SUBSTRATES

Fraction	*Cytidine-2',3'-phosphate*		*Uridine-2',3'-phosphate*		*Adenosine-2',3'-phosphate*		*Guanosine-2',3'-phosphate*	
	Extent of hydrolysis %	*Reaction products*	*Extent of hydrolysis* %	*Reaction products*	*Extent of hydrolysis* %	*Reaction products*	*Extent of hydrolysis* %	*Reaction products*
I	60	CMP-3'	80	UMP-3'	0	—	0	—
II	78	CMP-3'	65	UMP-3'	0	—	0	—
III	45	CMP-3'(-2')	40	UMP-3'(-2')	60	AMP-3'	15	GMP-3'
IV	10	CMP-3'(-2')	15	UMP-3'(-2')	20	AMP-3'	55	GMP-3'

Note. CMP-3', UMP-3', AMP-3' and GMP-3' are the 3'-derivatives of cytidylic, uridylic, adenylic and guanylic acid respectively.

DISCUSSION

In the present investigations, crystalline ribonuclease has been resolved into four major components by two-dimensional paper electrophoresis. The four components have been shown to possess difference in enzymic specificity.

Our analytical data indicated that each of the ribonuclease components is involved in the hydrolysis of specific internucleotide linkages; RNase I and RNase II liberated more uridylic acid and cytidylic acid, and demonstrated a greater enzymic activity on uridine-2',3'-phosphate and cytidine-2',3'-phosphate than either RNase III or RNase IV. Consequently, RNase III and RNase IV liberated more adenylic acid and guanylic acid from yeast ribonucleic acid, and demonstrated a greater enzymic activity on adenosine-2',3'-phosphate and guanosine-2',3'-phosphate than either RNase I or RNase II.

These variations in enzymic activities of the four major fractions, RNase I, II, III, and IV, provide strong evidence for the supposition that crystalline ribonuclease has different active fractions, each with its own specificity. Each specific fraction contributes to the hydrolysis of ribonucleic acid, and to the cleavage of specific internucleotide linkages in the ribonucleic acid molecule.

The mechanism of action of ribonuclease is not a simple hydrolysis but an intramolecular transphosphorylation followed by hydrolysis[16]. KUNITZ[7] demonstrated that the rate of hydrolysis is slower than the rate of transphosphorylation. The resolution of RNase into four active proteins indicated that each of the protein fractions isolated had two active sites, a transphosphorylation and an hydrolytic site. The electrophoretic resolution of one active protein into four fractions, each revealing a certain degree of specificity, suggested that the "active center" of biologically active proteins lies in some correct spatial configuration of polypeptide chains. Although this finding is in agreement with reports in the literature[17,18], it demonstrated specifically that certain polypeptides in an active protein molecule may reveal certain specific activities that could differ from the whole protein molecule activity, and thus the activity of the protein molecule is the resultant of activities of its polypeptide chains.

The degree of heterogeneity of the preparations studied depended upon the conditions employed in the isolation and crystallization of the enzyme, while quantitative amounts and proportions of the four major fractions revealed the age of the enzyme

(Table IV), and the degree of oxidation or reduction[19]. LEDOUX[20] has suggested that the chromatographic inhomogeneity of RNase might be attributed to different stages of oxidoreduction of its sulfur group[21,22].

TABLE IV

EFFECT OF AGING ON RIBONUCLEASE ELECTROPHORETIC HETEROGENEITY AND ENZYMIC ACTIVITY*

	Original %	*I*	*II*	*III*	*IV*	*Recovery* %
Fresh RNase solution	100	48	41	6.5	2.5	98
24 h RNase solution	100	46	40	5	3	96
48 h RNase solution	100	45	41.5	6	4.5	97
96 h RNase solution	100	44	40	7	5	96
192 h RNase solution	100	44	39	8	7	98
384 h RNase solution	100	42	40	9	6	97
768 h RNase solution	100	40	38	10	8	96
1536 h RNase solution	100	38	37	11	9	95

Note. The relative enzymic activity of fresh, 24, 48, 96, 192, 384, 768 and 1536 h solutions were 100, 99.9, 99.8, 99.8, 99.8, 99.6, 99.0, and 98.0 % of the original activity.

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* Crystalline "Armour" ribonuclease, recrystallized twice before use. Two per cent solution of crystalline "Armour" ribonuclease in a 25 ml flask. The surface of the solution was covered with 2 mm of mineral oil, thus protected from atmospheric contamination. At period intervals aliquots for enzyme assay, and for paper electrophoresis.

Ribonuclease activity was determined by following the optical density of methylene blue (0.20 g/ml) and ribonucleic acid (5 mg/ml) at 5500 A. as a function of time, after the addition of the different ribonuclease solution or fraction[23].

SUMMARY

1. Crystalline ribonuclease samples obtained from different commercial sources in addition to one prepared in the laboratory were resolved into their components, RNases I, II, III and IV, by a new two-dimensional electrophoretic technique.

2. RNase I and RNase II liberated more uridylic acid and cytidylic acid from yeast ribonucleic acid, and demonstrated a greater enzymic activity on uridine-2′,3′-phosphate and cytidine-2′,3′-phosphate, than either RNase III or RNase IV. RNase III and RNase IV liberated more adenylic acid and guanylic acid from yeast ribonucleic acid, and showed a greater enzymic activity on adenosine-2′,3′-phosphate and guanosine-2′,3′-phosphate than either RNase I and RNase II.

3. The degree of heterogeneity of the RNase samples studied revealed the age of the preparation.

4. It is thus demonstrated that certain of the activities of "crystalline ribonuclease" reside in four different protein entities, and some activity toward purine nucleotide esters existed in two of the four protein entities.

RÉSUMÉ

1. Des échantillons de ribonucléase cristallisée provenant soit du commerce, soit de préparations de laboratoire, sont décomposés par une nouvelle méthode d'électrophorèse sur papier, à deux dimensions, en ribonucléase I, II, III et IV.

2. Les ribonucléases I et II provoquent une augmentation de la quantité d'acide uridylique et d'acide cytidylique libérée à partir de l'acide ribonucléique de levure et montrent une plus grande activité enzymatique sur l'uridine-2′,3′-phosphate et sur le cytidine-2′,3′-phosphate que les ribonucléases III et IV. Les ribonucléases III et IV libèrent davantage d'acide adénylique et d'acide guanylique à partir de l'acide ribonucléique de levure et montrent une plus grande activité enzymatique sur l'adénosine-2′,3′-phosphate et sur le guanosine-2′,3′-phosphate que les ribonucléases I et II.

3. L'hétérogénéité de la ribonucléase étudiée révèle l'âge de la préparation.

4. Il a été démontré que certaines activités de la ribonucléase cristallisée rédisent dans 4 protéines différentes, et que son action à l'égard des esters des purines nucléotides est due à 2 seulement de ces protéines.

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ZUSAMMENFASSUNG

1. Verschiedene Handelspräparate sowie auch im Laboratorium hergestellte Proben von kristallisierter Ribonuklease wurden mit Hilfe einer neuen zweidimensionalen Elektrophoresemethode in ihre Bestandteile, Ribonuklease I, II, III und IV, gespalten.

2. Ribonuklease I und II setzen aus Hefe-Ribonukleinsäure mehr Uridyl- und Cytidylsäure in Freiheit und zeigen eine grössere enzymatische Aktivität gegenüber Uridin-2',3'-phosphat und Cytidin-2',3'-phosphat als Ribonuklease III und IV. Dagegen setzen diese beiden Letzteren mehr Adenyl- und Guanylsäure aus Heferibonukleinsäure in Freiheit und zeigen eine grössere enzymatische Aktivität gegenüber Adenosin-2',3'-phosphat und Guanosin-2',3'-phosphat als die beiden Ersteren.

3. Die Uneinheitlichkeit der untersuchten Ribonukleasepräparate war ein Mass für deren Alter.

4. Es wurde dargelegt, dass einige Aktivitäten der ,,kristallisierten Ribonuklease" zu vier verschiedenen Proteinen gehören und dass zwei von diesen vier Proteinen eine gewisse Aktivität gegenüber Purinnukleotidestern besitzen.

REFERENCES

[1] R. A. Alberty, E. A. Anderson and J. W. Williams, *J. Phys. & Colloid Chem.*, 82 (1948) 217.

[2] A. J. P. Martin and R. R. Porter, *Biochem. J.*, 49 (1951) 215.

[3] C. H. Hirs, W. H. Stein and S. More, *J. Am. Chem. Soc.*, 73 (1951) 1393; *J. Biol. Chem.*, 200 (1953) 493.

[4] D. M. Brown, D. I. Magrath and A. R. Todd, *J. Chem. Soc.*, (1952) 2703.

[5] R. Markham and J. D. Smith, *Biochem. J.*, 52 (1952) 552.

[6] L. A. Heppel, P. R. Whitfeld and R. Markham, *Biochem. J.*, 60 (1955) 8.

[7] M. Kunitz, *J. Gen. Physiol.*, 24 (1940) 15.

[8] A. A. Hakim, *Arch. Biochem. Biophys.*, 70 (1957) 591.

[9] A. A. Hakim, *Proc. Intern. Congr. Biochem., 3rd Congr., Brussels*, Section 8, (1955) 70.

[10] A. A. Hakim, *J. Biol. Chem.*, 225 (1957) 609.

[11] H. G. Kunkel and A. Tiselius, *J. Gen. Physiol.*, 35 (1951) 89.

[12] A. A. Hakim, *Enzymologia*, 17 (1956) 383.

[13] E. Magasanik, E. Vischer, R. Doniger, D. Elison and E. Chargaff, *J. Biol. Chem.*, 186 (1950) 37.

[14] J. Montreuil and P. Boulanger, *Compt. rend.*, 231 (1950) 247.

[15] R. Markham and J. D. Smith, *Biochem. J.*, 45 (1949) 294.

[16] G. Schmidt, in: E. Chargaff and J. N. Davidson, *The nucleic acids*, Vol. I., Academic Press, New York, 1955, p. 561.

[17] G. Kalnitsky and E. E. Anderson, *Biochim. Biophys. Acta*, 16 (1955) 302.

[18] G. Kalnitsky and W. I. Rogers, *Biochim. Biophys. Acta*, 20 (1956) 378.

[19] A. A. Hakim, *Biochim. Biophys. Acta*, 20 (1956) 581.

[20] L. Ledoux, *Biochem. Biophys. Acta*, 14 (1954) 267.

[21] S. R. Dickman, R. B. Knopf and J. B. Aboskar, *Abstr. 126th meeting Am. Chem. Soc.*, New York, 1954, 71 C.

[22] S. R. Dickman and J. B. Aboskar, *Federation Proc.*, 14 (1955) 207.

[23] D. Shugar, *Bull. acad. polon. sci.*, 1 (1953) 39.

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THE ABSORPTION SPECTRUM AND DISSOCIATION CONSTANTS OF 4-HYDROXYBENZTHIAZOLE

by

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4-Hydroxybenzthiazole and 8-hydroxyquinoline have the same reactive groupings, but the former shows a greater selectivity in its reactions with metal ions[1]. One of the main reasons that have been advanced for this behaviour is that 4-hydroxybenzthiazole is a stronger acid and a weaker base than 8-hydroxyquinoline[2]. In order to verify this statement the dissociation constants of 4-hydroxybenzthiazole were determined by a spectrophotometric method and confirmed by a potentiometric method. The spectrophotometric method, as in the case of 8-hydroxyquinoline, is dependent on the fact that the absorption spectrum of 4-hydroxybenzthiazole changes with the pH. The manner in which the absorption spectrum varied in different solvents, was investigated, for purposes of comparison with 8-hydroxyquinoline as well as for the identification of the ionic species present in solutions of varying pH.

EXPERIMENTAL

Preparation of compounds

4-Hydroxybenzthiazole was prepared by the method described by ERLENMEYER AND ÜBERWASSER[3]. The compound was recrystallized several times from 95% ethanol and had a melting point of 143°C. Benzthiazole (B.D.H. reagent grade), was purified by fractionating at 10 mm Hg-pressure. The fraction collected at 98°C was used for determining the absorption spectrum.

Absorption spectra

A Unicam Model S.P. 500 spectrophotometer was used for the determination of the absorption spectra in 1.00 cm cells. Slit widths from 0.4 to 1.5 mm were used as required. Measurements were made at a temperature of 27°C. Readings were taken at intervals of 1 mμ in the vicinity of the maxima and at intervals of 2 mμ elsewhere. 95% ethanol and standard solutions made from AnalaR HCl and NaOH were used as solvents.

Dissociation constants

A $3 \cdot 10^{-5} M$ solution of 4-hydroxybenzthiazole in buffers containing borate, phosphate, and acetate ions was used in the spectrophotometric method. Between pH 1.0 and 13.0 the ionic strength was kept constant at 0.10 by the addition of known amounts of KCl. The pH of the solutions was determined with the hydrogen electrode and an $N/10$ calomel electrode using a potentiometer reading to ± 0.002 V. The pH of the solutions in the extreme ranges between — 0.60 and 2.0 and 11.5 and 13.0 were calculated, and the solutions were made by adding measured volumes of standard HCl and NaOH. The extinction values for about thirty-five solutions of pH between — 0.60 and 13.0 were recorded at four different wavelengths, 240 mμ, 245 mμ, 225 mμ and 230 mμ. Fig. 1 shows the variation of the molar extinction coefficient with pH at the wavelengths 230 mμ and 240 mμ.

In the potentiometric method, the pH of solutions containing 4-hydroxybenzthiazole was de-

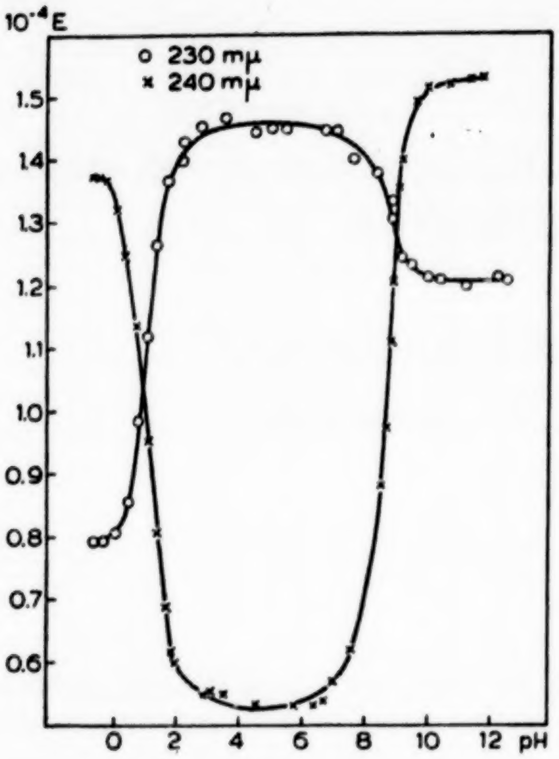

Fig. 1.

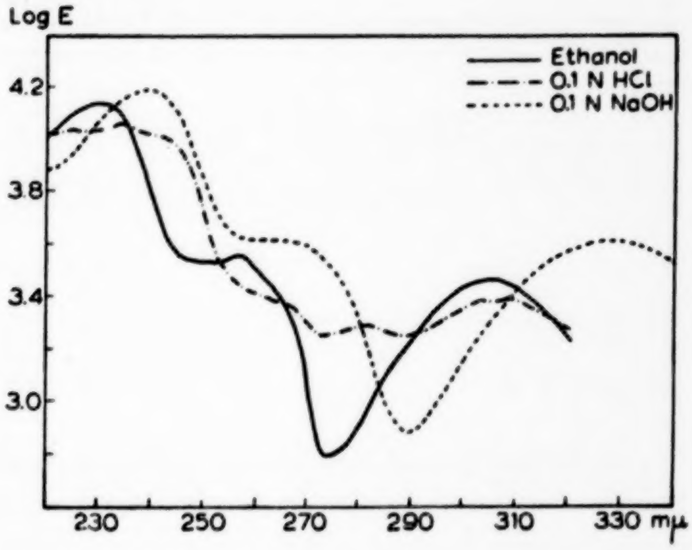

Fig. 2.

termined at 27°C. A saturated calomel electrode and a hydrogen electrode were used with a potentiometer reading to ± 0.002 V for determining the pH values of the solutions, which were prepared by adding calculated volumes of standard HCl and NaOH to predetermined amounts of 4-hydroxybenzthiazole.

RESULTS AND DISCUSSION

The absorption spectrum of 4-hydroxybenzthiazole shows bathochromic shifts both in acid and basic solution relative to ethanol (Fig. 2). This effect is similar to that observed with 8-hydroxyquinoline[4]. The absorption spectrum of 4-hydroxybenzthiazole, however, differs in two significant aspects from that of 8-hydroxyquinoline. Firstly, the former compound gives colourless solutions in acidic and basic solvents, and therefore, unlike 8-hydroxyquinoline, does not show an absorption in the visible region. Secondly, 4-hydroxybenzthiazole in neutral solvents such as ethanol has a characteristic maximum at 257 mμ; no corresponding maximum has been observed with 8-hydroxyquinoline in neutral solvents.

Fig. 3 shows the variation of the absorption spectrum of 4-hydroxybenzthiazole in solutions of HCl of 0.02N to 0.50N. A well defined maximum at 226 mμ is obtained in solutions of HCl up to about 0.04N, but in solutions of higher concentration the maximum becomes broader and ill-defined, until at a concentration of 0.20N, two distinct maxima, one at 223 mμ and the other at 240 mμ are obtained; at 236 mμ an isobestic point is present. It is probable that the maximum located at about 240 mμ is a result of the formation of the benzthiazolinium ion (c), and the bathochromic shift of the two main absorption bands relative to neutral ethanol is due to the several possible resonance forms that the ion (c) possesses. The broad absorption band present originally at 300-305 mμ suffers a bathochromic shift with increasing acid concentration and shows a definite bifurcation in all acid solutions. In this respect it is similar to the corresponding absorption maximum of benzthiazole (Fig. 4).

Since the absorption spectrum of 4-hydroxybenzthiazole changes with pH in the

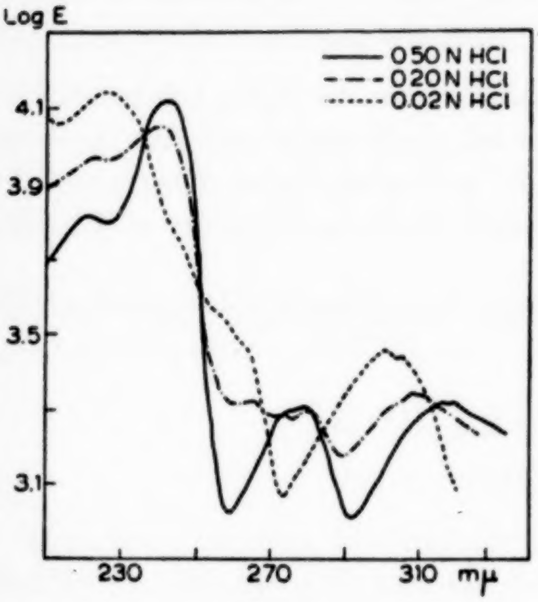

Fig. 3.

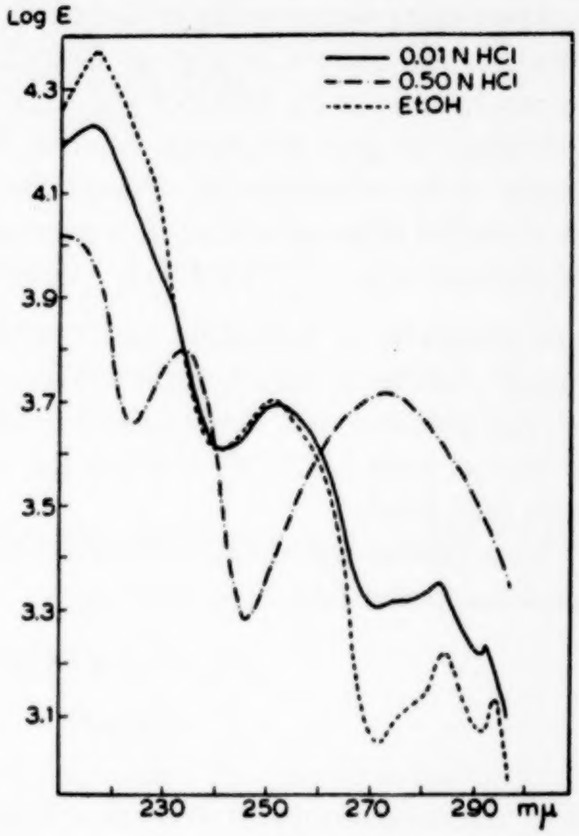

Fig. 4.

above manner, it is reasonable to postulate the following equilibria on the basis of the bathochromic shifts that are observed in passing from neutral to acid solvents and from neutral to basic solvents (Table I).

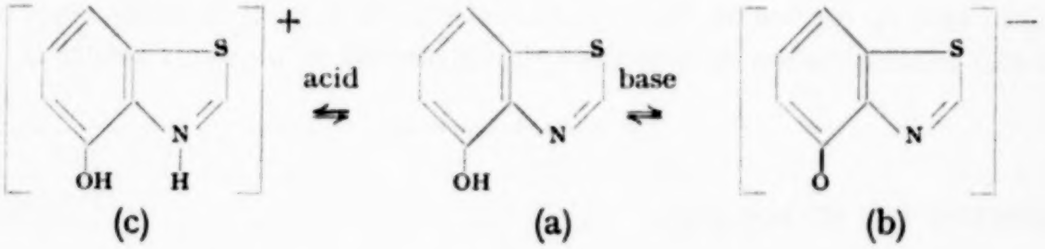

TABLE I

ABSORPTION MAXIMA IN THE SPECTRA OF 4-HYDROXYBENZTHIAZOLE, 8-HYDROXYQUINOLINE AND BENZTHIAZOLE

	In 0.10N HCl		*In ethanol*		*In 0.10N NaOH*	
	wavelength mμ	*log ε*[a]	*wavelength mμ*	*log ε*	*wavelength mμ*	*log ε*
4-Hydroxybenzthiazole	234	4.05	230	4.15	239	4.19
	281	3.29	257	3.63	328	3.62
	304—309[b]	3.38	305	3.53		
8-Hydroxyquinoline[9]	250	4.63	240	4.60	253	4.48
	309	3.20	308	3.47	335	3.44
	319	3.20			353	3.43
	358	3.22				
Benzthiazole	213	4.09	217	4.27		
	263	3.60	251	3.74		
	275[b]	3.60	285	3.23		
	277[b]	3.60	295	3.13		

[a] Molar extinction coefficients.

[b] Bifurcated maxima.

The absorption spectra of the parent compound benzthiazole in acidic and neutral solvents are shown in Fig. 4. Benzthiazole differs from quinoline since it shows a hypsochromic shift, and not the expected bathochromic shift that is observed with quinoline, in acid solutions, relative to ethanol. On the other hand, the absorption bands of benzthiazole in ethanol are located at approximately the same positions as those of thianaphthene in a neutral solvent. This is to be expected since the replacement of a $=\underset{|}{\mathrm{C}}-$ by a $=\mathrm{N}-$ does not usually affect the positions of the maxima. For example, in quinoline and naphthalene the absorption maxima are located at almost identical wavelengths[5]. The molar extinction coefficients and the positions of the maxima for benzthiazole in ethanol agree well with those determined by BOGGUST AND COCKER[6], but are not compatible with the measurements of LUTSKII AND SIDOROV[7].

In aqueous solutions, 4-hydroxybenzthiazole and its protonated form can lose protons in the following manner:

$$\begin{aligned} (\mathrm{C_7H_6ONS})^+ &\rightleftharpoons \mathrm{C_7H_5ONS} + \mathrm{H}^+ \\ \mathrm{C_7H_5ONS} &\rightleftharpoons (\mathrm{C_7H_4ONS})^- + \mathrm{H}^+ \end{aligned}$$

The dissociation constants of 4-hydroxybenzthiazole, K_1 and K_2, are defined as follows:

$$K_1 = c_n \cdot (\mathrm{H}^+)/c_a \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$K_2 = c_b \cdot (\mathrm{H}^+)/c_n \quad \ldots\ldots\ldots\ldots \quad (2)$$

where c_n, c_a and c_b represent the concentrations of (a), (c) and (b) respectively. If c is the total concentration of 4-hydroxybenzthiazole in aqueous solution, then

$$c = c_a + c_n + c_b \quad \ldots\ldots\ldots\ldots \quad (3)$$

From equations (1), (2) and (3):

$$c_a = c \Big/ \left\{1 + \frac{K_1}{(\mathrm{H}^+)} + \frac{K_1K_2}{(\mathrm{H}^+)^2}\right\}$$

$$c_b = c \Big/ \left\{1 + \frac{(\mathrm{H}^+)}{K_2} + \frac{(\mathrm{H}^+)^2}{K_1K_2}\right\}$$

$$c_n = c \Big/ \left\{1 + \frac{(\mathrm{H}^+)}{K_1} + \frac{K_2}{(\mathrm{H}^+)}\right\}$$

The total extinction E of a solution of concentration c is given by

$$\frac{E}{c} = \frac{e_a}{1 + \frac{K_1}{(\mathrm{H}^+)} + \frac{K_1K_2}{(\mathrm{H}^+)^2}} + \frac{e_n}{1 + \frac{(\mathrm{H}^+)}{K_1} + \frac{K_2}{(\mathrm{H}^+)}} + \frac{e_b}{1 + \frac{(\mathrm{H}^+)}{K_2} + \frac{(\mathrm{H}^+)^2}{K_1K_2}} \quad \ldots\ldots \quad (4)$$

Fig. 1 shows the molar extinction coefficients of 4-hydroxybenzthiazole at two different wavelengths plotted against the pH. Approximate values of K_1 and K_2 which

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can be obtained graphically[8], show that K_1/K_2 is of the order of 10^7. Hence equation (4) can be approximated to give equations (5) and (6) for calculating K_1 and K_2, respectively, from the observed molar extinction coefficients e_a, e_b, and e_n, of the acid, base, and neutral forms of 4-hydroxybenzthiazole.

$$\frac{E}{c} = \frac{(\mathrm{H}^+)\cdot e_a + K_1\cdot e_n}{K_1 + (\mathrm{H}^+)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\frac{E}{c} = \frac{(\mathrm{H}^+)\cdot e_n + K_2\cdot e_b}{K_2 + (\mathrm{H}^+)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The values of the dissociation constants of 4-hydroxybenzthiazole obtained by the spectrophotometric method are as follows:

$$\mathrm{p}K_1 = 1.20 \pm 0.05 \text{ and } \mathrm{p}K_2 = 8.85 \pm 0.05$$

The potentiometric method used to confirm these values for the dissociation constants, depends on the measurements of the pH of solutions in which c_a/c_n and c_n/c_b are approximately equal to unity.

$$\mathrm{pH} = \mathrm{p}K_1 + \log\frac{c_a}{c_n} \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$\mathrm{pH} = \mathrm{p}K_2 + \log\frac{c_n}{c_b} \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

In equation (7), $$\frac{c_a}{c_n} = \frac{(A) - (B) - (\mathrm{H}^+)}{c - (A) + (B) + (\mathrm{H}^+)} \ldots\ldots\ldots\ldots\ldots (9)$$

In equation (8), $$\frac{c_n}{c_b} = \frac{c - (B) + (A) + K_w/(\mathrm{H}^+)}{(B) - (A) - K_w/(\mathrm{H}^+)} \ldots\ldots\ldots\ldots (10)$$

where c = concentration of 4-hydroxybenzthiazole in solution,
(A) = concentration of HCl added,
(B) = concentration of NaOH added,
K_w = ionic product of water.

The individual terms in equations (9) and (10) are suitably adjusted in order to make the factors c_a/c_n and c_n/c_b approximately unity. By this potentiometric method $\mathrm{p}K_1 = 1.3$ and $\mathrm{p}K_2 = 8.7$, for 4-hydroxybenzthiazole.

ACKNOWLEDGEMENTS

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SUMMARY

The absorption spectra of 4-hydroxybenzthiazole and the parent compound, benzthiazole, have been determined in acidic, basic and neutral solutions, and compared with the corresponding absorption spectra of 8-hydroxyquinoline and quinoline. The dissociation constants of 4-hydroxybenzthiazole obtained by a spectrophotometric method as well as a potentiometric method, show that it is a stronger acid and a weaker base than 8-hydroxyquinoline.

RÉSUMÉ

Les spectres d'absorption du 4-hydroxybenzothiazole et du composé voisin, le benzothiazole, ont été déterminés en solutions acide, basique et neutre, et comparés avec les spectres d'absorption correspondants de la 8-hydroxyquinoléine et de la quinoléine.

Les constantes de dissociation de 4-hydroxybenzothiazole obtenues par méthode spectrophotométrique aussi bien que par méthode potentiométrique, montrent que c'est un acide plus fort, et une base plus faible que la 8-hydroxyquinoléine.

ZUSAMMENFASSUNG

Die Absorptionsspektren des 4-Oxybenzthiazols und des verwandten benzthiazols wurden in saurer, basischer und neutraler Lösung bestimmt und mit den entsprechenden Spektren des 8-Oxychinolins und des Chinolins verglichen. Die spektrophotometrisch und auch potentiometrisch bestimmten Dissoziationskonstanten des 4-Oxybenzthiazols zeigen, dass dieses eine stärkere Säure und schwächere Base ist als das 8-Oxychinolin.

REFERENCES

[1] H. Erlenmeyer and E. H. Schmidt *Helv. Chim. Acta*, 24 (1941) 1159.
[2] F. Feigl, *Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949, p. 194.
[3] H. Erlenmeyer and H. Überwasser, *Helv. Chim. Acta*, 25 (1942) 515.
[4] G. W. Ewing and E. A. Steck, *J. Am. Chem. Soc.*, 68 (1946) 2181.
[5] R. A. Morton and A. J. A. de Gouveia, *J. Chem. Soc.*, (1934) 916.
[6] W. A. Boggust and W. Cocker, *ibid.*, (1949) 355.
[7] A. E. Lutskii and I. A. Sidorov, *J. Gen. Chem. U.S.S.R.*, 17 (1947) 141.
[8] W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, 30 (1926) 1683.
[9] T. Moeller and F. L. Pundsack, *J. Am. Chem. Soc.*, 76 (1954) 647.

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THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

PART III. THE NITROAMINONAPHTHALENE MONOSULPHONIC ACIDS AS SPOT TESTS FOR STANNOUS TIN

by

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INTRODUCTION

In earlier papers of this series, the qualitative and quantitative applications of 6-nitro-2-aminonaphthalene-8-sulphonic acid as a reagent for tin have been reported[1,2]. Three isomers of 6-nitro-2-aminonaphthalene-8-sulphonic acid have been synthesized and found to be of value in the detection of stannous tin. Spots of aqueous solutions of 48 metal salts were placed on Whatman chromatographic paper No. 1 and sprayed separately with aqueous solutions of each of the nitroaminonaphthalene monosulphonic acids. Of all metal ions tested, only stannous tin gave an intense fluorescence when viewed under ultraviolet light, after the quenching of any previous fluorescence by treatment with 15N NH_4OH. The compounds used were 8-nitro-2-aminonaphthalene-6-sulphonic acid (ammonium salt) and the potassium salts of two isomeric acids prepared by the mononitration of 2-aminonaphthalene-5-sulphonic acid*.

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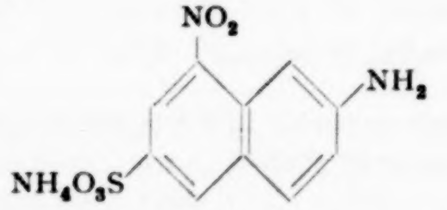
* On study leave at Birkbeck College, University of London.

EXPERIMENTAL

Preparation of reagents

8-Nitro-2-aminonaphthalene-6-sulphonic acid. A modification of the method of VOROSHCOV AND GRIBOV[3] was used. Urea (0.25 g) was dissolved in concentrated H_2SO_4 (30 ml) followed by 2-aminonaphthalene-6-sulphonic acid (7.8 g) and the reaction mixture chilled to 0°C by the direct addition of dry ice. Nitrating acid, consisting of a mixture of 2.5 ml HNO_3 (sp.gr. 1.42) and 3.5 ml H_2SO_4 (sp.gr. 1.84) was added at 0°C over a period of one hour, the reaction mixture stirred for a further half hour, then poured onto 200 g of crushed ice. The precipitate was treated with a slight excess of concentrated NH_4OH, the solution chilled to 0°C, and the ammonium salt (8.2 g) filtered. This material was purified by recrystallisation from 50% aqueous alcohol and crystallised in pale orange-red needles which were very soluble in water.

Analysis

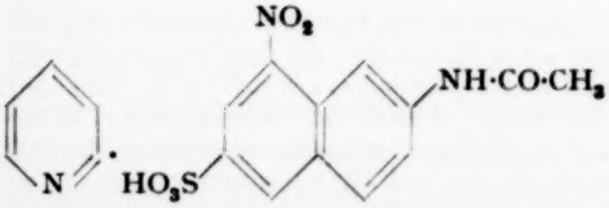


$C_{10}H_{11}O_5N_3S$:
Calculated: C, 42.10; H, 3.89; N, 14.73.
Found: C, 41.95; H, 3.89; N, 14.30.

Pyridinium acetyl derivative of 8-nitro-2-aminonaphthalene-6-sulphonic acid. CHEN AND CROSS[4] have identified the aminonaphthalene monosulphonic acids through their pyridinium acetyl derivatives. A modification of this procedure has been applied to the characterisation of 8-nitro-2-aminonaphthalene-6-sulphonic acid. The dry ammonium salt (0.15 g) of this acid was mixed to a paste with pyridine (0.2 ml) then acetylated with acetic anhydride (0.4 ml). The mixture was refluxed for five minutes, cooled and the pale yellow needles of the pyridinium acetyl derivative recrystallised from 90% aqueous alcohol.

M.p. = 239 - 40°C.

Analysis



$C_{17}H_{15}O_6N_3S$
Calculated: C, 52.43; H, 3.88; pyridine, 20.31.
Found: C, 52.27; H, 3.87; pyridine, 20.25.

Pyridine analysis was carried out using the procedure recommended by CHEN AND CROSS[4] whereby an aqueous solution of the pyridinium salt is titrated with standard NaOH at room temperature, using phenolphthalein as indicator.

Nitration of 2-aminonaphthalene-5-sulphonic acid. The 2-aminonaphthalene-5-sulphonic acid (16.5 g), dissolved in concentrated H_2SO_4 (275.0 ml) containing urea (6.5 g), was nitrated at 0°C with a mixture of 5.8 ml HNO_3 (sp.gr. 1.42) and 9.0 ml H_2SO_4 (sp.gr. 1.84) in a procedure similar to that used for 2-aminonaphthalene-6-sulphonic acid. After the nitrating acid had been added, the mixture was stirred for a further half hour, then poured into an equal volume of ice water. More water was added slowly at 0°C until the concentration of H_2SO_4 was approximately 12*N*. At this point, the major product of the reaction (isomer I) precipitated and was filtered, the minor product (isomer II) remaining in the filtrate. The pink precipitate (I) was washed with hot water and the residue treated with a minimum of saturated aqueous $KHCO_3$. The resulting potassium salt of nitro-2-aminonaphthalene-5-sulphonic acid (isomer I) was recrystallised from hot water in yellow needles.

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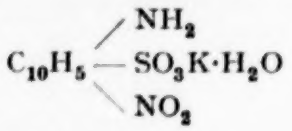
* Degradation studies are being carried out at present to determine the position of the nitro group in each of the two nitro-2-aminonaphthalene-5-sulphonic acids.

Analysis. Isomer I — potassium salt



$$C_{10}H_5\begin{array}{l}\diagup NH_2\\ — SO_3K\cdot H_2O\\ \diagdown NO_2\end{array}$$

$C_{10}H_9O_6N_2SK$

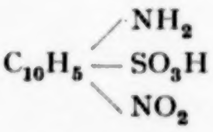
Calculated: C, 37.03; H, 2.80; K, 12.06.

Found: C, 36.93; H, 2.60; K, 12.30.

The potassium salts of these nitroaminonaphthalene sulphonic acids usually crystallise with one or two moles of water of crystallisation. This water renders formation of a characteristic pyridinium acetyl derivative difficult. The ammonium salts are usually anhydrous and are preferable salts for the preparation of derivatives.

Careful acidification of the potassium salt of isomer I yields pale yellow needles of the free acid which is purified by recrystallisation from hot water.

Analysis. Isomer I — free acid



$$C_{10}H_5\begin{array}{l}\diagup NH_2\\ — SO_3H\\ \diagdown NO_2\end{array}$$

$C_{10}H_8O_5N_2S$

Calculated: C, 44.78; H, 3.01; N, 10.45.

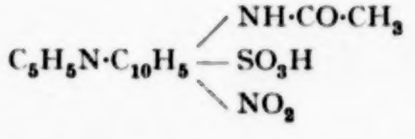
Found: C, 44.66; H, 3.15; N, 10.65.

The ammonium salt prepared by neutralizing the free acid with 15*N* NH_4OH is very soluble in water and crystallises in yellow needles from 50% aqueous alcohol.

Pyridinium acetyl derivative of isomer I. This compound was prepared using the modified CHEN AND CROSS[4] procedure already described. The derivative was purified by recrystallisation from 95% aqueous alcohol, and crystallised in pale yellow needles.

M.p. 212°C.

Analysis



$$C_5H_5N\cdot C_{10}H_5\begin{array}{l}\diagup NH\cdot CO\cdot CH_3\\ — SO_3H\\ \diagdown NO_2\end{array}$$

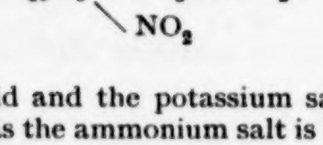
$C_{17}H_{15}O_6N_3S$

Calculated: Pyridine, 20.31.

Found: 20.15.

Isomer II from nitration reaction. The filtrate remaining, after the removal of isomer I from the crude nitration mixture (*i.e.* 12*N* H_2SO_4), was treated with $CaCO_3$ and $Ca(OH)_2$ to convert the nitroaminonaphthalene sulphonic acid to its calcium salt and remove residual sulphuric acid as $CaSO_4$. The precipitated $CaSO_4$ was washed well with boiling water and the combined filtrate and washings concentrated to one third previous volume. A saturated aqueous solution of Na_2CO_3 was added and the precipitated $CaCO_3$ filtered and washed with hot H_2O. Concentration of the filtrate yielded orange-red crystals of the sodium salt of isomer II which was recrystallised from hot water.

Analysis. Isomer II — sodium salt.



$$C_{10}H_5\begin{array}{l}\diagup NH_2\\ — SO_3Na\cdot 2H_2O\\ \diagdown NO_2\end{array}$$

$C_{10}H_{11}O_7N_2SNa$

Calculated: C, 38.96; H, 2.94; Na, 7.46.

Found: C, 38.77; H, 2.84; Na, 7.31.

The free acid and the potassium salts of this nitro-2-aminonaphthalene-5-sulphonic acid are yellow, whereas the ammonium salt is bright red and is used for the preparation of the pyridinium acetyl derivative.

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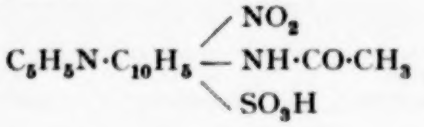
Pyridinium acetyl derivative of isomer II. The modified CHEN AND CROSS[4] procedure yielded a derivative which crystallised from 95% alcohol in yellow needles.

M.p. 260-1°C.

Analysis



$$C_5H_5N{\cdot}C_{10}H_5\begin{cases}NO_2\\ NH{\cdot}CO{\cdot}CH_3\\ SO_3H\end{cases}$$

$C_{17}H_{15}O_6N_3S$

Calculated: C, 52.43; H, 3.88; Pyridine, 20.31.

Found: C, 52.22; H, 3.80; Pyridine, 20.20.

The melting points of the pyridinium acetyl derivatives of the three nitro-aminonaphthalene monosulphonic acids are quite different and serve as ideal derivatives for the characterisation of the particular acids.

Technique of spot testing

Spots of aqueous solutions measuring 0.01 ml which contained 0.1 mg of each of the metal ions, were placed on a sheet of Whatman chromatographic paper No. 1 and sprayed separately with 0.1% aqueous solutions of the reagents. The sheets were air-dried for 15 minutes and viewed under ultraviolet light, any fluorescence being noted. The sheets were now sprayed with 15*N* NH_4OH, air-dried, and again viewed under ultraviolet light, the quenching of any previous fluorescence being noted. The reagents employed are listed in Table I.

TABLE I

REAGENTS USED FOR SPRAYING OF METAL IONS

1. 0.1% aqueous solution of the ammonium salt of 8-nitro-2-aminonaphthalene-6-sulphonic acid.
2. 0.1% aqueous solution of the potassium salt of isomer I from the nitration of 2-aminonaphthalene-5-sulphonic acid.
3. 0.1% aqueous solution of the potassium salt of isomer II from the nitration of 2-aminonaphthalene-5-sulphonic acid.

RESULTS

The results obtained are shown in Table II.

Sensitivity tests for stannous tin were carried out, 2 ml of 30% hypophosphorous acid being added per 100 ml of dilute tin solution in order to prevent atmospheric oxidation. Spots containing 0.01 ml of the various dilute stannous chloride solutions were placed on sheets of Whatman chromatographic paper No. 1, sprayed separately with 0.2% aqueous solutions of reagent numbers 1, 2 and 3 and of the ammonium salt of 6-nitro-2-aminonaphthalene-8-sulphonic acid. Using the same test procedure as previously described, it was found that reagent numbers 1, 2 and 3 were each capable of detecting 10^{-8} g of stannous tin, whilst the 0.2% solution of the ammonium salt of 6-nitro-2-aminonaphthalene-8-sulphonic acid was capable of detecting 10^{-7} g. The fluorescent spots of stannous tin were found to be greenish-blue on treatment with 6-nitro-2-aminonaphthalene-8-sulphonic acid (ammonium salt), greenish-yellow with reagent number 2 and blue with both reagent numbers 1 and 3. The ammonium salt of 6-nitro-2-aminonaphthalene-8-sulphonic acid was found to give the most intensely fluorescent spots, followed in order of decreasing intensity of fluorescence by reagent numbers 3, 1 and 2. Spots of 2% hypophosphorous acid were used in blank tests and no fluorescence was observed under these conditions.

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TABLE II

RESULTS OBTAINED FROM SPRAYING SPOTS OF METALLIC IONS WITH VARIOUS REAGENTS BEFORE AND AFTER QUENCHING OF FLUORESCENCE WITH 15*N* NH_4OH

Metal ion	*Reagent number*					
	1		*2*		*3*	
	before quenching	*after quenching*	*before quenching*	*after quenching*	*before quenching*	*after quenching*
Fe^{+2}	F		F		F	
Fe^{+3}						
Sn^{+2}	F	F (intense blue)	F	F (intense yellow-green)	F	F (intense blue)
Sn^{+4}	F		F	F (trace)	F	
Hg^{+}	F				F	
Hg^{+2}	F				F	
As^{+3}	F		F	F (trace)	F	
As^{+5}						
Sb^{+3}	F	F (trace)	F	F (trace)	F	
Bi^{+3}	F	F (trace)	F	F (trace)	F	
Al^{+3}			F		F	
Cr^{+3}						
Mn^{+2}						
Zn^{+2}						
Sr^{+2}						
Ca^{+2}						
Ba^{+2}						
Mg^{+2}						
Cu^{+2}	F (trace)					
Co^{+2}						
Ni^{+2}						
Pb^{+2}						
Na^{+}						
K^{+}						
Rb^{+}						
Cs^{+}						
Li^{+}						
Ce^{+3}	F				F	
Ce^{+4}	F (halo)		F		F (halo)	
Mo^{+6}						
Pt^{+2}	F (halo)		F (halo)	F (slight halo)	F (halo)	
Pt^{+4}						
Au^{+3}	F (halo)	F (trace)			F (halo)	
Pd^{+2}						
Tl^{+}						
Tl^{+3}	F		F (halo)	F (slight halo)	F (halo)	
W^{+6}						
Be^{+2}	F		F		F	
UO_2^{+2}						
VO^{+2}	F		F		F	
V^{+5}						
Th^{+4}						
ZrO^{+2}	F				F (trace)	
Ru^{+3}	F (halo)					
Ti^{+3}	F	F (trace)			F	F (trace)
Ti^{+4}						
Cd^{+2}						
Ag^{+}						

F = fluoresces; F (halo) = faint fluorescent ring around a nonfluorescent spot.

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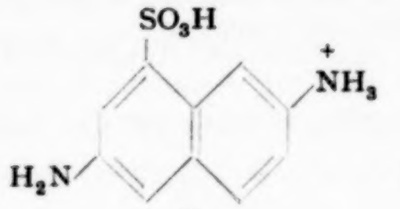
DISCUSSION

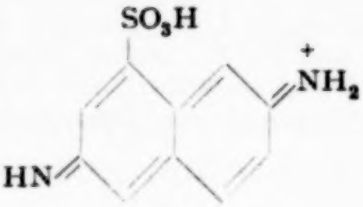
When 6-nitro-2-aminonaphthalene-8-sulphonic acid is used as a fluorimetric reagent for stannous tin, it has been shown that the compound responsible for the fluorescence is a salt of 2,6-diaminonaphthalene-8-sulphonic acid[1,2].

Three further nitroaminonaphthalene monosulphonic acids give positive results in the fluorimetric tin test, and the compounds responsible for the fluorescence are salts of the corresponding diaminonaphthalene monosulphonic acids.

Since these salts are colourless, this substantiates the theory that the fluorescence is due to the excited state of the naphthyl ammonium ion (structure I) and not the highly conjugated imino form (structure II).



(I)



(II)

This theory for the fluorescence has been based on the data available from the use of four nitroaminonaphthalene monosulphonic acids as reagents. It is proposed to carry out further experimental work using nitroaminonaphthalene monosulphonic acids in which the nitro group is *meta* to the amino group. If the fluorescence can be attributed to the excited state of the imino form (II) and not structure(I),then *meta*-nitro-substituted acids will *not* be expected to yield a fluorimetric tin test, since their corresponding diaminonaphthalene monosulphonic acids are not capable of quinonoid contributions such as is exhibited by (II).

It is of interest also to note that all four nitroaminonaphthalene monosulphonic acids used in this series of tests will detect approximately the same concentration of stannous tin (10^{-7} to 10^{-8} g), but 6-nitro-2-aminonaphthalene-8-sulphonic acid gives the most intense fluorescence of all isomers.

In future experiments, it is not proposed to restrict the test to nitroaminonaphthalene monosulphonic acids alone but to use other nitro systems in order to find the most sensitive analytical reagent for fluorimetric tin determinations.

ACKNOWLEDGEMENT

One of us (J.R.A.A.) wishes to thank Professor W. WARDLAW for permission to carry out part of this work at the Department of Chemistry, Birkbeck College, University of London.

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SUMMARY

Three new reagents, *viz.* 8-nitro-2-aminonaphthalene-6-sulphonic acid (ammonium salt) and the two nitroaminonaphthalene sulphonic acids (potassium salts) prepared by the mononitration of 2-aminonaphthalene-5-sulphonic acid have been developed as spot tests for stannous tin. Each reagent produces a strong fluorescence under ultraviolet light, less than one microgram of stannous tin being detected under the conditions of test. The application of the reagents to the quantitative estimation of tin is also indicated.

RÉSUMÉ

Trois nouveaux réactifs: l'acide 8-nitro-2-aminonaphtalène-6-sulfonique (en son sel d'ammonium) et les deux acides nitroaminonaphtalène sulfoniques (en leurs sels de potassium), préparés par mononitration de l'acide 2-aminonaphtalène-5-sulfonique sont utilisés comme "spot tests" pour

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la détermination de l'étain(II). Chacun des réactifs produit une vive fluorescence en lumière ultraviolette, moins de 1 μg d'étain(II) pouvant être identifié dans les conditions de l'essai. On indique également l'application de ces réactifs au dosage quantitatif de l'étain.

ZUSAMMENFASSUNG

Drei neue Reagenzien, nämlich 8-Nitro-2-aminonaphtalin-6-sulfosäure (Ammoniumsalz) und die beiden bei der Mononitrierung von 2-Aminonaphtalin-5-sulfosäure entstehenden Nitroaminonaphtalinsulfosäuren (Kaliumsalze) wurden als Tüpfelreagenzien für zweiwertiges Zinn entwickelt. Jedes dieser Reagenzien gibt, bei Beobachtung in ultraviolettem Licht eine starke Fluoreszenz. Unter den Bedingungen der Probe kann weniger als 1 μg zweiwertiges Zinn nachgewiesen werden. Die Anwendung der Reagenzien zur quantitativen Zinnbestimmung wird ebenfalls umschrieben.

REFERENCES

[1] J. R. A. Anderson and J. L. Garnett, *Anal. Chim. Acta*, 8 (1953) 393.
[2] J. R. A. Anderson and S. Lenzer-Lowy, *ibid.*, 15 (1956) 246.
[3] N. N. Voroshcov and K. A. Gribov, *Bull. inst. polytech. Ivanovo-Voznesensk*, 7 (1923) 109 [through *C.A.*, 18 (1924) 1124].
[4] P. Chen and E. J. Cross, *J. Soc. Dyers Colourists*, 59 (1943) 144.

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CHELATOMETRISCHE BESTIMMUNG VON ZINK-, CADMIUM- UND BLEIIONEN IN ANWESENHEIT VON VARIAMINBLAU ALS REDOXINDIKATOR

von

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Zur Bestimmung des Endpunktes chelatometrischer Titrationen wurden schon mehrere Methoden ausgearbeitet. Schwarzenbach[1] verwendete in seinen ersten Arbeiten Säure-Basenindikatoren zur Endpunktsbestimmung. In späteren Mitteilungen wird über verschiedene elektrometrische Endpunktsindikationsmöglichkeiten berichtet. Die weitverbreitete Anwendung der Chelatometrie wurde jedoch in der Praxis erst durch die Einführung der sogenannten Metallindikatoren (chelatbildende Farbstoffe) ermöglicht. In den letzten Zeiten werden immer häufiger Redoxindikatoren zur Endpunktsbestimmung chelatometrischer Titrationen herangezogen[2,3,4]. Bei der Titration oxydierender Lösungen, wie z.B. im Falle von Eisen(III)-Lösung, liegt die Anwendung von Redoxindikatoren auf der Hand. Bei der chelatometrischen Titration von nicht oxydierenden Ionen können vermittelnde Redoxsysteme gebraucht werden[5,6,7,8]. Die Selektivität der chelatometrischen Titrationen kann mit geeigneter Wasserstoffionenkonzentration noch erhöht werden. Die meisten von den bis zur dieser Zeit gebrauchten chelatometrischen Indikatoren funktionieren nur reversibel im alkalischen Gebiet. Beachtenswert sind jedoch auch die in saurem Medium reversibel funktionierenden chelatometrischen Indikatoren. Von den in saurem Gebiet gebrachten Indikatoren sind die Redoxindikatoren diejenigen, die am meisten gebraucht werden können. Als vermittelndes Redoxsystem lässt sich das System Kaliumhexacyanoferrat(II)-Kalium-

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hexacyanoferrat(III) vorteilhaft verwenden. Diese Indikationsmethode wurde zuerst von BROWN UND HAYES[5] in die Chelatometrie eingeführt, indem sie Zinkionen in Anwesenheit des von BELCHER UND NUTTEN[9] empfohlenen 3,3'-Dimethylnaphtidin (Redoxindikator) titrierten. Ein Nachteil dieser Methode liegt darin, dass der Umschlag im Endpunkt sich sehr verzögert, und die Lösung nach Zugabe jedes einzigen Tropfens 15 Sekunden lang geschüttelt werden muss. Um diesen Nachteil zu beseitigen, führten FLASCHKA UND FRANSCHITZ[6] ein indirektes Bestimmungsverfahren ein, wobei sie die überschüssige ÄDTA-Lösung mit Zinksalzlösung zurücktitrierten. Ein ähnliches Verfahren arbeitete SAJÓ[7,8] unter Anwendung von Benzidin als Redoxindikator aus. Wir fanden unterdessen, dass das Variaminblau auch in diesem Falle mit gutem Erfolg als Redoxindikator angewendet werden kann. Verwendet man diesen Indikator dann liegt eine Möglichkeit zur direkten Titration, und zwar mit der üblichen Titrationsgeschwindigkeit, vor. Ausserdem ist das mit Variaminblau durchgeführte Bestimmungsverfahren dem mit Benzidin durchgeführten gegenüber auch deswegen vorteilhafter, weil die Sulfationen, die mit Benzidin einen Niederschlag bilden, dabei nicht störend einwirken.

Fig. 1 stellt das Umschlagspotential des Variaminblaus[10] (4-Amino-4'-methoxydiphenylamin) und den Potentialwert des Redoxsystems Hexacyanoferrat(II)-Hexacyanoferrat(III) als Funktion der pH-Werte dar. Wie aus der Figur ersichtlich, lässt sich der Indikator in diesem Falle in der Nähe des pH-Wertes 5 anwenden. Die zu titrierenden Schwermetallionen bilden mit den Hexacyanoferrat(II)-Ionen einen schwerlöslichen Niederschlag (oft nur in einer mit dem Auge nicht erfassbaren Menge), wodurch sich das Redoxpotential des Systems in die positive Richtung verschiebt und der Indikator seine violette Oxydationsfarbe aufnimmt. Bei beendeter Titration bildet das Äthylendiamintetraacetat mit dem Metallion einen beständigen Komplex. Im Falle von Zinkionen z.B. erhöht sich das pZn — bei pH 5 — von 5 auf 7, der Niederschlag löst sich auf und die Konzentrationsverhältnisse des Systems Hexacyanoferrat(II)-Hexacyanoferrat(III) ändern sich. Demzufolge verschiebt sich das Redoxpotential sprunghaft in die negative Richtung und der Indikator wird farblos.

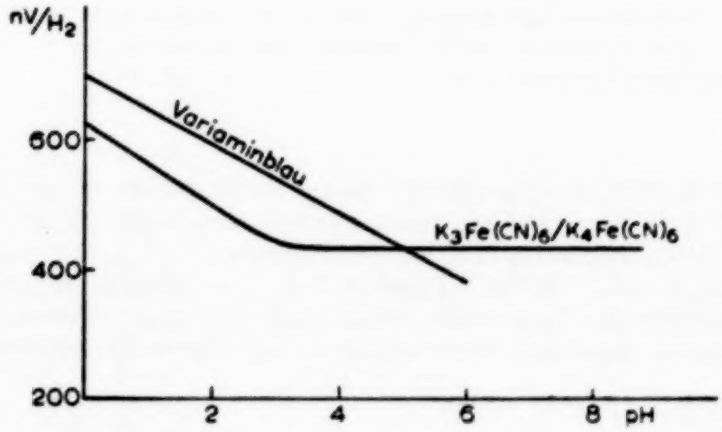

Fig. 1.

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BESTIMMUNG VON ZINK-, BLEI- UND CADMIUMIONEN

In unseren früheren Arbeiten[11] titrierten wir die Zink- und Bleiionen unter Anwendung von Variaminblau als Indikator mit Ascorbinsäure- bzw. Kaliumhexacyanoferrat(II)-masslösung. Die Endpunktsbestimmung beruht auch bei den chelatometrischen Titrationen auf demselben Prinzip. Es wird der pH-Wert der Lösung nach Neutralisation mit einem geeigneten Puffer (z.B. Acetat) auf 5 eingestellt, und nach Zugabe des Indikators und des aus Kaliumhexacyanoferrat(II)-Kaliumhexacyanoferrat(III) bestehenden Gemisches wird die Lösung mit ÄDTA-Lösung bis zum Verschwinden der violetten Farbe titriert.

Angewendete Lösungen

Die *Zink-* bzw. *Cadmiumsulfatlösung* wurde aus krist. Zink- bzw. Cadmiumsulfat p.a. bereitet. Ihr Titer wurde als Zinkammoniumphosphat bzw. Cadmiumammoniumphosphat bestimmt.

Zur Bereitung der *Bleinitratlösung* wurde das Bleimetall p.a. in Salpetersäure gelöst. Ihr Wirkungswert wurde in Form von Bleisulfat bestimmt.

Als *Indikatorlösung* diente die frisch bereitete 1%-ige wässrige Lösung von Variaminblau B (4-Amino-4′-methoxy-diphenylamin-HCl).

Gemisch von Kaliumhexacyanoferrat(II) und *Kaliumhexacyanoferrat(III)*. Die 0.1*M* $K_3[Fe(CN)]_6$-Lösung wurde mit 3.29 g krist. Salz versetzt und nach Auflösen auf 100 ml ergänzt. Die 0.1*M* $K_4[Fe(CN)_6]$-Lösung wurde mit 4.22 g krist. $K_4[Fe(CN)_6]\cdot 3H_2O$ versetzt und ebenfalls auf 100 ml verdünnt. Die 0.1*M* Kaliumhexacyanoferrat(III)- und Kaliumhexacyanoferrat(II)-Lösungen wurden in einem Verhältnis von 1:4 gemischt. Es empfiehlt sich die Mischung der Lösungen unmittelbar vor der Titration durchzuführen. In dunkler Flasche sind beide Lösungen monatenlang titerbeständig.

*0.05*M *ÄDTA-Lösung*. 18.613 g des p.a. Salzes wurden auf 1 l gelöst. Ihr Titer wurde mit Magnesiumsulfatlösung titrimetrisch kontrolliert.

*0.2*M *Natriumacetat-Essigsäure-Pufferlösung*. 19.2 g Natriumacetat wurden in 29.5 ml 0.2*M* Essigsäurelösung gelöst. Das Gemisch wurde sodann mit Wasser auf 1 l verdünnt. Der pH-Wert der so bereiteten Lösung ergab sich zu 5.00.

Arbeitsvorschrift

Die Blei, Zink oder Cadmium in unbekannter Menge enthaltende, in 200 ml Kolben befindliche Lösung wird mit 50 ml 0.2*M* Acetat-Essigsäure-Pufferlösung vom pH-Wert 5, dann mit 0.5 ml 1%-iger Variaminblau-Indikatorlösung und schliesslich mit 1-2 Tropfen Kaliumhexacyanoferrat(II)-Kaliumhexacyanoferrat(III)-Gemisch versetzt. Die violettfärbige Lösung wird bis zur Farblosigkeit titriert. In der Nähe des Endpunktes muss langsam titriert werden. Sollte die Lösung auf 50-60°C erwärmt werden, so kann die Titration auch rasch beendet werden.

TABELLE I

DIE GENAUIGKEIT DER TITRATION ALS FUNKTION DER ZU BESTIMMENDEN ZINKMENGE IN 0.05N LÖSUNGEN

Einwaage 0.05M $ZnSO_4$-Lsg. *ml*	*Verbrauch an 0.05M ÄDTA-Lsg.* *ml*	*Mittelwert* *ml*	*Abweichung vom Sollwert* *ml*	%
10.17	10.23 10.20 10.21	10.21	+ 0.04	+ 0.4
20.50	20.62 20.60 20.61	20.61	+ 0.11	+ 0.5
30.90	31.05 31.05 31.02	31.04	+ 0.08	+ 0.4

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TABELLE II

DIE GENAUIGKEIT DER TITRATION ALS FUNKTION DER ZU BESTIMMENDEN BLEIMENGE IN $0.05N$ LÖSUNGEN

Einwaage $0.05M$ $Pb(NO_3)_2$-*Lsg.* *ml*	*Verbrauch an* $0.05M$ *ÄDTA-Lsg.* *ml*	*Mittelwert* *ml*	*Abweichung vom Sollwert* *ml*	%
4.96	5.00 4.98 4.96	4.98	+ 0.02	+ 0.5
10.00	9.97 9.95 9.93	9.95	— 0.05	— 0.5
20.10	19.90 19.95 19.95	19.93	— 0.17	— 0.8
30.03	30.00 29.95 29.97	29.97	— 0.06	— 0.2

TABELLE III

DIE GENAUIGKEIT DER TITRATION ALS FUNKTION DER ZU TITRIERENDEN CADMIUMMENGE IN $0.05N$ LÖSUNGEN

Einwaage $0.05M$ $CdSO_4$-*Lsg.* *ml*	*Verbrauch an* $0.05M$ *ÄDTA-Lsg.* *ml*	*Mittelwert* *ml*	*Abweichung vom Sollwert* *ml*	%
10.21	10.05 10.03 10.06	10.05	— 0.16	— 1.6
20.42	20.42 20.40 20.39	20.40	— 0.02	— 0.1
30.63	30.55 30.62 30.60	30.59	— 0.04	— 0.1
51.05	51.02 51.12 51.02	51.04	— 0.01	— 0.02

PRAKTISCHE ANWENDUNGSMÖGLICHKEITEN

Die Genauigkeit der Methode lässt sich aus den Analysenergebnissen der Tabellen I, II und III beurteilen.

Ein grosser Vorteil der Methode liegt darin, dass Zink-, Cadmium- und Bleiionen direkt und neben Alkali- und Erdalkalimetallen chelatometrisch bestimmt werden können, da die Stabilitätskonstanten der Letzteren von der Grössenordnung 10^8 sind und demzufolge die Titration nicht beeinflussen. Ein jedes der erwähnten Ionen kann auch neben Magnesiumionen bestimmt werden. Letztere können in derselben Lösung nach Zugabe von Ammoniumchlorid-Ammoniumhydroxyd-Pufferlösung und in Anwesenheit von Eriochromschwarz T als Indikator auch selbst bestimmt werden.

Die Methode kann mit Vorteil zur Analyse von Bleilegierungen verwendet werden. Es ist möglich die Bestimmungsdauer der Bleiionen zu verkürzen, wenn die in Sulfatform getrennten Bleiionen zu im Essigsäure lösliches Carbonat umgesetzt und wie

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oben titriert werden. Der Bleisulfatniederschlag wird dekantiert so, dass die Hauptmenge des Niederschlages im Kolben zurückbleibt. Der Niederschlag wird vom Filterpapier mit heissem Ammoniumacetat abgelöst und in den Kolben zurückgebracht. Nach Zugabe von 40 ml 0.5*M* Natriumcarbonatlösung wird das Gemisch 20-30 Minuten auf dem Wasserbade erwärmt. Die Lösung wird von dem sich schnell absetzenden Niederschlag abgegossen und durch ein feinporöses Filterpapier filtriert. Die Hauptmenge des im Kolben verbleibenden Niederschlages wird dekantiert. Die auf dem Filterpapier verbliebenen Niederschlagsreste werden mit heisser, in einem Verhältnis von 1:1 verdünnter Eissigsäure abgelöst und in den Kolben zurückgebracht. Nach vollständiger Auflösung des Niederschlages wird die Lösung gegen Phenolphtalein als Indikator mit 1*N* Natriumhydroxydlösung neutralisiert und nach Zugabe der Puffer- und Indikatorlösungen wie oben beschrieben titriert.

Es wurde versucht auch die Kupfer-, Nickel- und Manganionen auf die beschriebene Weise zu bestimmen, aber im Falle von Kupfer und Nickel wurden wegen der intensiven Farbe der Komplexverbindungen, im Falle von Mangan dagegen wegen der beträchtlichen Löslichkeit des Manganeisen(II)cyanids, keine befriedigende Ergebnisse erzielt.

ZUSAMMENFASSUNG

Es wurde zur Bestimmung der Zink-, Cadmium- und Bleiionen ein direktes chelatometrisches Verfahren ausgearbeitet. Die Bestimmung lässt sich unter Anwendung des Redoxsystems Kaliumhexacyanoferrat(II)-Kaliumhexacyanoferrat(III) und des Variaminblau-Redoxindikators bei pH 5 mit befriedigender Genauigkeit durchführen. Magnesium, Barium, Strontium und Calcium stören das Bestimmungsverfahren nicht. In Zink-, Blei- oder Cadmiumionen enthaltender Lösung kann mit Hilfe von Eriochromschwarz T Indikator auch das Magnesium bestimmt werden.

SUMMARY

A direct chelatometric method for the determination of zinc, cadmium and lead ions was developed. Using the redox systems potassium ferrocyanide-potassium ferricyanide and Variamine Blue as redox indicator, the determination could be carried out at pH 5 with sufficient accuracy. Magnesium, barium, strontium and calcium do not disturb the determination. In solutions containing zinc, lead or cadmium ions, magnesium can also be determined when Eriochrome Black T is used as the indicator.

RÉSUMÉ

On a mis au point un procédé chélatométrique direct de dosage des ions zinc, cadmium et plomb. Le dosage se pratique avec une précision satisfaisante grâce au système rédox hexacyanoferrate(II) tétrapotassique-hexacyanoferrate(III) tripotassique, en employant le bleu de variamine comme indicateur rédox, au pH 5. Le magnésium, le baryum, le strontium et le calcium ne gênent pas. Dans une solution contenant des ions zinc, plomb ou cadmium, le magnésium peut être également dosé à l'aide du noir d'ériochrome T comme indicateur.

LITERATUR

[1] G. Schwarzenbach und W. Biedermann, *Helv. Chim. Acta*, 31 (1948) 159, 331, 456.
[2] L. Erdey und G. Rády, *Z. anal. Chem.*, 149 (1956) 250.
[3] H. Flaschka, *Mikrochim. Acta*, (1954) 361.
[4] P. Wehber, *Z. anal. Chem.*, 149 (1956) 244.
[5] E. G. Brown und T. J. Hayes, *Anal. Chim. Acta*, 9 (1953) 6.
[6] H. Flaschka und W. Franschitz, *Z. anal. Chem.*, 144 (1955) 421.
[7] I. Sajó, *Magyar Kém. Folyóirat*, 60 (1954) 268, 333.
[8] I. Sajó, *Magyar Kém. Folyóirat*, 62 (1956) 56.
[9] R. Belcher, A. J. Nutten und W. I. Stephen, *J. Chem. Soc.*, (1951) 1520.
[10] L. Erdey und A. Bodor, *Z. anal. Chem.*, 137 (1952/53) 410.
[11] L. Erdey und L. Pólos, *Z. anal. Chem.*, 153 (1956) 401, 413.

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APPLICATION DE LA CHÉLATOMÉTRIE AU DOSAGE DU FLUOR DANS LES COMPOSÉS ORGANIQUES

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HISTORIQUE ET PRINCIPE

L'emploi des composés organiques fluorés devient de plus en plus fréquent et il nous a semblé qu'une méthode simple et rapide du dosage du fluor dans ces produits présenterait un intérêt appréciable.

Les méthodes rapides de décomposition des fluorures organiques actuellement en vogue, si l'on excepte les procédés de combustion ou de pyrolyse sous courant d'hydrogène[1] ou de vapeur d'eau avec ou sans oxygène[2], font appel au potassium ou au sodium métalliques[3,4,5] ou au peroxyde de sodium[6,7]. La destruction est totale dans les deux cas et le fluor passe quantitativement à l'état de fluorure alcalin.

Nous avons choisi la méthode de WURZSCHMITT[6] au peroxyde de sodium parce qu'elle est plus facile à manier.

Les procédés de dosage volumétrique du fluorure alcalin obtenu sont assez délicats à mettre en oeuvre et reposent, soit sur la formation de chloro- ou bromo-fluorure de plomb[8] ou plus souvent sur l'emploi, en présence d'un indicateur tel que l'alizarine sulfonate de sodium, des sels de thorium ou de zirconium[4,5,7,9], d'aluminium ou de cérium[11]. On sait que les fluorures peuvent être précipités quantitativement sous forme de sels de calcium et que le précipité obtenu peut servir à leur détermination gravimétrique[12]; la filtration est très facile si l'on opère en présence d'ions acétiques; il y a lieu, bien entendu d'éviter la précipitation de carbonate de calcium en chassant par ébullition le gaz carbonique contenu dans l'eau et les solutions aqueuses utilisées.

La seule méthode volumétrique basée sur cette précipitation, à notre connaissance, est celle de SCOTT[13] qui employe une solution d'acétate de calcium dont il précipite l'excès de calcium sous forme d'oxalate, lequel est ensuite mesuré par une solution de permanganate de potassium; ce procédé exige deux précipitations et demande un temps d'exécution assez long; la modification de UEBEL[13] qui laisse ensemble les deux précipités remédie en partie à cet inconvénient, mais les résultats obtenus sont faussées par suite de la formation d'oxalate de calcium à partir du fluorure de calcium comme l'a observé GEYER[12]. Nous avons pensé qu'il serait plus intéressant, après élimination du fluorure par filtration, de mesurer directement l'excès de calcium, au moyen de l'éthylènediaminotétracétate disodique dont l'emploi pour le dosage du calcium est maintenant bien connu[14,15].

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RÉACTIFS NÉCESSAIRES

Peroxyde de sodium. Ce produit est maintenant en vente courante sur le marché. La présence de carbonate de sodium ne gène pas dans les conditions du dosage.

Mono-éthylène-glycol. Ce produit est également devenu tout à fait courant; nous avons choisi de préférence un corps sec mais toutefois nous avons constaté que la présence d'une légère humidité n'était pas gênante.

Acide acétique. Nous avons employé la qualité cristallisable.

Noir Ériochrome à 0.2%. Ce réactif est obtenu en dissolvant 0.2 g de Noir Ériochrome T dans 100 ml de triéthanolamine; il y a lieu de le conserver bien bouché.

Réactif magnésien. Ce réactif est préparé en pesant:

éthylène-diaminotétracétate magnéso-disodique (complexonate de magnésium)	4 g
chlorure d'ammonium	11 g
cyanure de sodium	0.1 g
ammoniaque concentré	70 ml
eau distillée fraîchement bouillie Q.S.P.	200 ml

(Le cyanure de sodium est destiné à complexer le nickel pouvant provenir de l'attaque du corps de la bombe.)

Chélate disodique M/50. On pèse 7.4 g d'éthylène-diaminotétracétate-disodique (complexon III) qu'on dissout dans un peu d'eau distillée fraîchement bouillie et complète à un litre avec cette même eau. On conserve en flacon Pyrex bien bouché. Si on prend soin d'utiliser un produit pur et préalablement séché vers 45-50°C jusqu'à poids constant, il n'est pas nécessaire de déterminer la normalité de la solution autrement que par le calcul suivant

$$N_c' = \frac{P}{372.2}$$

P = Poids de chélate utilisé.

On peut toutefois, si on le préfère, déterminer cette normalité par étalonnage à partir d'un échantillon de carbonate de calcium de titre connu dissout dans l'acide chlorhydrique[14].

Chlorure de calcium M/5. On dissout 30 g de chlorure de calcium pur cristallisé ($CaCl_2 \cdot 2H_2O$) dans un litre d'eau distillée fraîchement bouillie. On conserve bien bouché. La normalité du réactif est mesurée de la façon suivante:

On prélève au moyen d'une pipette 25 ml qu'on laisse couler dans une fiole jaugée de 250 ml et complète à 250 ml au moyen d'eau distillée fraîchement bouillie, on agite pour homogénéiser la solution et prélève, au moyen d'une pipette, 25 ml qu'on laisse couler dans une fiole d'Erlenmeyer et auxquels on ajoute 10 ml de réactif magnésien mesurés à la pipette et quelques gouttes de Noir Ériochrome à 0.2% préparé comme ci-dessus; on chauffe vers 50°C et laisse couler la solution de chélate $M/50$ au moyen d'une burette jusqu'à virage du rouge au bleu (ce virage est assez net, mais assez lent à ce produire et il y a lieu d'opérer lentement à la fin de ce dosage); la normalité de la solution est donnée par la formule

$$N_K' = \frac{V_c \times N_c'}{25}$$

V_c = nombre de ml de solution de chélate utilisé,
N_c' = normalité de la solution de chélate.

MODE OPÉRATOIRE

Dans une bombe de 10 ml en nickel, on pèse dans l'ordre 0.15 à 0.30 g de mono-éthylène-glycol (*Note a*), un poids p de substance (*Note b*) et 8 g de peroxyde de sodium; on ferme la bombe et chauffe le fond avec une petite flamme jusqu'à ce que le claquement habituel se soit fait entendre, ce qui se produit généralement au bout de quelques secondes. On laisse refroidir puis ouvre et place le corps de la bombe dans un bécher avec 50 cc d'eau distillée après avoir rincé le couvercle plusieurs fois; on porte progressivement à ébullition jusqu'à cessation de dégagement gazeux puis laisse refroidir et transvase dans une fiole jaugée de 250 ml en Pyrex. On rince plusieurs fois le bécher et le corps de la bombe à l'eau distillée, puis ajoute goutte à goutte de l'acide acétique de façon à amener le pH entre 4 et 5 qu'on mesure au papier indicateur; on ajoute de l'eau distillée pour amener le volume du liquide à 150 ml environ, et porte à ébullition pendant quelques minutes; on vérifie le pH et ramène celui-ci entre 4 et 5 s'il a remonté. On maintient l'ébullition et ajoute de l'acide acétique autant qu'il est nécessaire pour que le pH ne remonte plus, c'est à dire jusqu'à élimination du gaz carbonique; on laisse couler alors, au moyen d'une pipette, 25 ml de chlorure de calcium $M/5$ dans le liquide à ébullition; on refroidit à température ambiante et complète à 250 ml au moyen d'eau distillée fraîchement bouillie; on filtre rapidement (*Note c*) et prélève, au moyen d'une pipette, 25 ml du filtrat auxquels on ajoute 10 cc de réactif magnésien exactement mesurés et quelques gouttes de Noir Ériochrome à 0.2%; on chauffe vers 50°C et coule le chélate disodique $M/50$ au moyen d'une burette jusqu'à virage du rouge au bleu en prenant les précautions qui ont été indiquées pour l'étalonnage de la solution de chlorure de calcium; la teneur en % en fluor dans l'échantillon analysé est donné par la formule

$$T_F = \frac{19 \times V}{p}$$

où

$V = 5\,N_K' - 2\,V'\,N_c'$,
N_K' = normalité de la solution de chlorure de calcium,
V' = nombre de ml de chélate utilisé,
N_c' = normalité du chélate.

Note (a). Pour les corps particulièrement riches en fluor nous avons observé qu'il était nécessaire d'augmenter la quantité de mono-éthylène-glycol indiqué par WURZSCHMITT[6], jusqu'à 0.30 g pour obtenir une minéralisation totale de la substance.

Note (b). Le poids p est calculé de façon à contenir 0.003-0.005 atome-gramme de fluor, mais sans toutefois dépasser 0.30 g.

Note (c). Le précipité de fluorure de calcium obtenu dans les conditions opératoires indiquées est cristallin et la filtration se fait facilement sans qu'il soit nécessaire d'ajouter aucun agent de floculation.

RÉSULTATS OBTENUS

Nous avons essayé la présente technique sur divers produits fluorés nettement différents, tant au point de vue teneur en fluor (17-75%) qu'au point de vue solidité de la molécule, et parmi lesquels nous avons fait figurer un échantillon de poly-tétrafluoro-éthylène ou Téflon provenant des usines DU PONT DE NEMOURS et trois échantillons de *p*-fluorotoluène, *a,a,a*-trifluorotoluène et acide trifluoro-acétique des usines EASTMAN-KODAK. Les résultats sont donnés dans le Tableau I.

TABLEAU I

Nature	*Poids* g	*Teneur trouvée* %	*Teneur calculée* %
p-Fluorotoluène	0.294	17.1	17.2
(Ébullit. 116-117°C)	0.303	17.0	—
	0.299	17.0	—
a,a,a-Trifluorotoluène	0.142	38.5	39.0
(Ébullit. 100-102°C)	0.138	38.6	—
	0.147	38.4	—
Acide trifluoro-acétique	0.117	49.7	50.0
(Ébullit. 71-73°C)	0.128	49.6	—
	0.122	49.6	—
Poly-tétrafluoro-éthylène	0.104	75.1	75.8
	0.113	74.9	—
	0.129	74.8	—

RÉSUMÉ

Le fluor combiné dans les corps organiques peut être dosé volumétriquement, après décomposition au peroxyde de sodium, par précipitation au moyen d'une solution de chlorure de calcium dont on mesure l'excès par chélatométrie.

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SUMMARY

Fluorine bound in organic matter can be determined volumetrically, after decomposition with sodium peroxide, by precipitation by means of a calcium chloride solution, the excess of which is measured chelatometrically.

ZUSAMMENFASSUNG

Organisch gebundener Fluor kann volumetrisch bestimmt werden; nach Zersetzung mit Natriumperoxyd fällt man mit einer Calciumchloridlösung, deren Überschuss chelatometrisch gemessen wird.

BIBLIOGRAPHIE

[1] G. Cadenbach, *Angew. Chem.*, 46 (1933) 130.
[2] R. O. Teston et F. E. McKenna, *Anal. Chem.*, 19 (1947) 193.
W. C. Schumb et K. J. Radimer, *Anal. Chem.*, 20 (1948) 871.
O. I. Milner, *Anal. Chem.*, 21 (1949) 311.
O. I. Milner, *Anal. Chem.*, 22 (1950) 315.
H. S. Clark, *Anal. Chem.*, 23 (1951) 659.
J. M. Salsbury, J. W. Cole, L. G. Overholser, A. R. Armstrong et J. H. Yoe, *Anal. Chem.*, 23 (1951) 603.
R. R. Rickard, F. L. Bail et W. W. Harris, *Anal. Chem.*, 23 (1951) 919.
[3] J. F. Miller, H. Hunt et E. T. McBee, *Anal. Chem.*, 19 (1947) 148.
R. H. Kimball et L. E. Tufts, *Anal. Chem.*, 19 (1947) 150.
R. Belcher et J. C. Tatlow, *Analyst*, 76 (1951) 592.
[4] M. O. Korshun, V. A. Klimova et M. N. Chumachenko, *Zhur. Anal. Khim.*, 10 (1955) 358.
G. Kainz et F. Scholler, *Mikrochim. Acta*, 4-6 (1956) 843.
E. J. H. Des, *Mikrochim. Acta*, 4-6(1956) 858.
[5] A. I. Savchenko, *Zhur. Anal. Khim.*, 10 (1955) 355.
[6] M. L. Nichols et J. S. Olsen, *Ind. Eng. Chem., Anal. Ed.*, 15 (1943) 342.
N. B. Chapman, R. Heap et B. C. Sanders, *Analyst*, 73 (1948) 434.
B. Wurzschmitt, *Chemiker-Ztg.*, 74 (1950) 356.
B. Wurzschmitt et W. Zimmermann, *Fortschr. chem. Forsch.*, 1 (1950) 485.
B. Wurzschmitt, *Mikrochemie*, 36 (1951) 769.
[7] G. Eger et A. Yarden, *Anal. Chem.*, 28 (1956) 512.
[8] G. Starck, *Z. anorg. Chem.*, 70 (1911) 173.
I. Tananajew, *Z. anal. Chem.*, 99 (1934) 21.
F. Specht, *Z. anorg. u. allgem. Chem.*, 231 (1937) 181.
P. Ehrlich et G. Pietzka, *Z. anal. Chem.*, 131 (1951) 84.
[9] J. H. de Boer et J. Basart, *Z. anorg. u. allgem. Chem.*, 152 (1926) 203.
H. H. Willard et O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, 5 (1933) 7.
W. D. Armstrong, *J. Am. Chem. Soc.*, 55 (1933) 1741.
D. Dahle, R. V. Bonnar et H. J. Wichmann, *J. Assoc. Offic. Agr. Chemists*, 21 (1938) 459.
F. J. McClure, *Ind. Eng. Chem., Anal. Ed.*, 11 (1939) 171.
J. W. Hammond et W. H. MacIntire, *J. Assoc. Offic. Agr. Chemists*, 23 (1940) 398.
M. P. Matuszak et D. R. Brown, *Ind. Eng. Chem., Anal Ed.*, 17 (1945) 100.
J. P. Branciaroli et J. G. Coleman, *Anal. Chem.*, 28 (1956) 803.
S. K. Datta, *Z. anal. Chem.*, 149 (1956) 333.
D. F. Adams et R. K. Koppe, *Anal. Chem.*, 28 (1956) 116.
[10] A. K. Babko et T. N. Nazarchuk, *Ukrain. Khim. Zhur.*, 20 (1954) 678.
R. Kojima, S. Nagase et H. Muramatsu, *Bunseki Kagaku (Japan Analyst)*, 4 (1955) 518.
R. Schliebs, *Z. anal. Chem.*, 150 (1956) 321.
[11] A. Kurtennacker et W. Jurenka, *Z. anal. Chem.*, 82 (1930) 210.
G. Batchelder et M. Meloche, *J. Am. Chem. Soc.*, 53 (1931) 2131.
[12] J. Berzelius, *Ann. chim. et phys.*, 3 (1816) 34.
F. P. Treadwell et A. A. Koch, *Z. anal. Chem.*, 43 (1904) 469.
R. J. Meyer et W. Schulz, *Angew. Chem.*, 38 (1925) 203.
R. Geyer, *Z. anorg. u. allgem. Chem.*, 252 (1943) 42.
[13] W. W. Scott, *Ind. Eng. Chem., Anal. Ed.*, 46 (1924) 703.
W. Uebel, *Chemiker-Ztg.*, 49 (1925) 701.
[14] G. Schwarzenbach et W. Biedermann, *Chimia (Switz.)*, 2 (1948) 56.
H. Diehl, C. A. Goetz et C. C. Hach, *J. Am. Water Works Assoc.*, 42 (1950) 40.
E. Leroi et J. A. Gautier, *Ann. pharm. franç.*, 11 (1953) 329.
G. Schwarzenbach, *Die komplexometrische Titration*, Ferdinand Enke Verlag, Stuttgart, 1955.

[15] W. BIEDERMANN ET G. SCHWARZENBACH, *Chimia (Switz.)*, 2 (1948) 1.
J. D. BETZ ET C. A. NOLL, *J. Am. Water Works Assoc.*, 42 (1950) 49.
J. J. CONNERS, *J. Am. Water Works Assoc.*, 42 (1950) 33.
C. A. GOETZ, T. C. LOOMIS ET H. DIEHL, *Anal. Chem.*, 22 (1950) 798.
K. KNIE, *Österr. Wasserwirtsch.*, 4 (1952) 13.
G. R. BOTHA ET M. M. WEBB, *J. Inst. Water Engrs.*, 6 (1952) 459.
J. BANKS, *Analyst*, 77 (1952) 484.
M. BROOKE ET M. HOLBROOK, *Chemist Analyst*, 41 (1952) 80.
P. SOUCHAY ET M. CRAIZON, *Bull. soc. chim. France*, (1952) (no. 1) 34.
S. I. SINYAKOVA, *Zhur. Anal. Khim.*, 10 (1955) 139.
A. BAROCCIO ET C. NIGRO, *Ann. sper. agrar.* (Rome), 10 (1956) 119.
J. PATTON ET W. REEDER, *Anal. Chem.*, 28 (1956) 1926.
M. FRIEDRICH ET M. FÁBORSKÝ, *Československ. sklář a keramik*, 6 (1956) 114.
Z. HOST'IALEK ET M. POLLERTOVA, *Chem. průmysl*, 6 (1956) 271.
J. KRIZOVA, *Stavivo*, 34 (1956) 239.

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DIETHYLENETETRA-AMMONIUM SULPHATOCERATE AS VOLUMETRIC REAGENT

V. DETERMINATION OF ORGANIC DERIVATIVES OF HYDRAZINE BY THE IODINE MONOCHLORIDE METHOD

by

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B. SINGH *et al.*[1] have prepared diethylenetetra-ammonium sulphatocerate, $[Ce(NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_2](SO_4)_2{\cdot}2H_2SO_4{\cdot}7H_2O$, and used it as an oxidimetric standard in volumetric analysis. B. SINGH *et al.*[2] have used potassium metaperiodate, sodium metavanadate, chloramine-B, chloramine-T and diethylenetetra-ammonium sulphatocerate for the oxidation of hydrazine to nitrogen and water with a four-electron change.

$$N_2H_4 + 2\,O = N_2 + 2H_2O$$

MCBRIDE, HENRY AND SKOLNIK[3] have shown that the hydrazino group in monosubstituted hydrazines, their hydrazones, and acyl derivatives, is oxidised with a four-electron change to nitrogen with potassium iodate in both hydrochloric and sulphuric acid solutions. The reduction of iodate to iodine monochloride takes place in hydrochloric acid and to iodine in sulphuric acid.

$$N_2H_5^+ + IO_3^- + H_3O^+ + Cl^- = ICl + N_2 + 4H_2O$$
$$5N_2H_5^+ + 4IO_3^- = 5N_2 + 11H_2O + H_3O^+ + 2I_2$$

The nature and proportions of the end-products of the oxidation of hydrazine and its derivatives vary with the specific nature and the oxidation-reduction potential of the oxidising system and with the pH of the medium.

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B. SINGH AND S. S. SAHOTA[4] have used sodium metavanadate for the volumetric estimation of some organic derivatives of hydrazine. Each hydrazino group in these compounds is oxidised with a four-electron change to nitrogen and water. In the present investigation diethylenetetra-ammonium sulphatocerate has been used for the volumetric determination of semicarbazide hydrochloride, benzalazine, benzalsemicarbazone, aminoguanidine hydrochloride, chloralhydrazine, *p*-methoxybenzalsemicarbazone, *o*-chlorobenzalsemicarbazone and acetonesemicarbazone. In the presence of hydrochloric acid these derivatives of hydrazine react with diethylenetetra-ammonium sulphatocerate in accordance with the equations:

$$4\mathrm{Ce}^{+4} + \mathrm{NH_2CONH.NH_2} + \mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + (\mathrm{C_6H_5CH{:}N\text{-}})_2 + 2\mathrm{H_2O} = 4\mathrm{Ce}^{+3} + 2\mathrm{C_6H_5CHO} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + \mathrm{C_6H_5CH{:}N.NHCONH_2} + 2\mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{C_6H_5CHO} + \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + \mathrm{HN{:}C(NH.NH_2)NH_2} + \mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{HN{:}C(OH)NH_2} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + \mathrm{CCl_3.CH(OH)NH.NH_2} + \mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{CCl_3.CH(OH)_2} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + \mathrm{CH_3O.C_6H_4CH{:}N.NHCONH_2} + 2\mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{CH_3O.C_6H_4CHO} + \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + \mathrm{Cl.C_6H_4CH{:}N.NHCONH_2} + 2\mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{Cl.C_6H_4CHO} + \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{N_2} + 4\mathrm{H}^+$$

$$4\mathrm{Ce}^{+4} + \mathrm{(CH_3)_2C{:}N.NHCONH_2} + 2\mathrm{H_2O} = 4\mathrm{Ce}^{+3} + \mathrm{(CH_3)_2CO} + \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{N_2} + 4\mathrm{H}^+.$$

EXPERIMENTAL

The organic derivatives of hydrazine were prepared by well known methods. Diethylenetetra-ammonium sulphatocerate was prepared by the method of B. SINGH *et al.*[1] and its standard solution (0.02*N*) was obtained by dissolving its known weight in 2*N* sulphuric acid solution and making up to a known volume with the acid.

A known amount of the hydrazine derivative was transferred to a conical flask, and about 25 ml of water, 60 ml of concentrated hydrochloric acid, 5 ml of 0.02*M* iodine monochloride and 5 ml of chloroform were added. The mixture was cooled to room temperature and titrated with 0.02*N* diethylenetetra-ammonium sulphatocerate solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired a purple colour due to iodine. The conical flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the sulphatocerate solution was continued, shaking vigorously after each addition until the chloroform layer was faintly violet. The sulphatocerate solution was then added dropwise, with shaking after the addition of each drop, until the chloroform layer became very pale yellow. The end-point was very sharp.

In these titrations, normality of the solution with respect to hydrochloric acid was kept between 6*N* to 7*N*. Several titrations were performed in each case. From the volume of diethylenetetra-ammonium sulphatocerate used, corresponding to the end-point in each titration, the amount of each substance was calculated. The results showed that 0.005 g to 0.032 g of the substances as listed above can be determined by using diethylenetetra-ammonium sulphatocerate as a volumetric oxidising agent.

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The author thanks Mr. S. S. SAHOTA for preparing the organic derivatives of hydrazine.

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SUMMARY

Diethylenetetra-ammonium sulphatocerate has been used as an oxidising agent in hydrochloric acid medium for the volumetric determination of semicarbazide hydrochloride, benzalazine, benzalsemicarbazone, aminoguanidine hydrochloride, chloralhydrazine, *p*-methoxybenzalsemicarbazone, *o*-chlorobenzalsemicarbazone and acetonesemicarbazone, using iodine monochloride as a catalyst and preoxidiser. Chloroform was used as an indicator. It was coloured violet owing to the liberation of iodine during the titration and became very pale yellow at the end-point owing to the formation of iodine monochloride. Each hydrazino group in these compounds was oxidised quantitatively with a four-electron change to nitrogen with diethylenetetra-ammonium sulphatocerate as an oxidant in hydrochloric acid solution.

RÉSUMÉ

Le sulfato-cérate de diéthylènetétra-ammonium est utilisé comme agent oxydant en milieu chlorhydrique pour le dosage volumétrique du chlorhydrate de semicarbazide, de la benzalazine, de la benzalsemicarbazone, du chlorhydrate d'aminoguanidine, de la chloralhydrazine, de la *p*-méthoxybenzalsemicarbazone, de l'*o*-chlorobenzalsemicarbazone et de l'acétonesemicarbazone, en utilisant le monochlorure d'iode comme catalyseur et agent préoxydant. Le chloroforme est utilisé comme indicateur. On a une coloration violette due à la libération de l'iode pendant la titration qui vire au jaune pâle à la fin à cause de la formation de monochlorure d'iode.

Chaque groupement hydrazino des composés est oxydé quantitativement par un échange de quatre électrons à l'azote avec le sulfatocérate de diéthylènetétra-ammonium comme oxydant en milieu d'acide chlorhydrique.

ZUSAMMENFASSUNG

Das Diäthylentetraammoniumsulfatocerat wurde als Oxydationsmittel in salzsaurem Milieu zur volumetrischen Bestimmung der folgenden Substanzen benutzt: Semicarbazidhydrochlorid, Benzalazin, Benzalsemicarbazon, Aminoguanidinhydrochlorid, Chloralhydrazin, *p*-Methoxybenzalsemicarbazon, *o*-Chlorobenzalsemicarbazon und Acetonsemicarbazon. Monochlorjod wurde als Katalysator und Voroxydationsmittel benutzt, Chloroform als Indikator. Letzteres war durch das bei der Titration in Freiheit gesetzte Jod violett und wurde am Endpunkt schwach gelb, durch Bildung von Monochlorjod. Die Hydrazingruppen dieser Verbindungen wurden im Laufe einer Vier-Elektronen-Umsetzung quantitativ zu Stickstoff oxydiert, wobei das Diäthylentetraammoniumsulfatocerat in salzsaurer Lösung als Oxydationsmittel diente.

REFERENCES

[1] BALWANT SINGH AND S. SINGH, *Anal. Chim. Acta*, 14 (1956) 109.

[2] BALWANT SINGH *et al.*, *J. Indian Chem. Soc.*, 29 (1952) 34; *Anal. Chim. Acta*, 9 (1953) 22; 10 (1954) 408; 11 (1954) 313; 13 (1955) 301; 14 (1956) 109.

[3] W. R. MCBRIDE, R. A. HENRY AND S. SKOLNIK, *Anal. Chem.*, 25 (1953) 1042.

[4] BALWANT SINGH AND S. S. SAHOTA, *Anal. Chim. Acta*, 17 (1957) 285.

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PAPER CHROMATOGRAPHY OF METAL COMPLEXES
PART II. REPLACEMENT ABILITY OF THE LIGANDS*

by

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In a previous paper[1] we studied the roles of the metal and of the ligand in the formation of coördination compounds between some bi- and polyvalent cations and acetic acid and its three chloro derivatives. On the basis of further experimental work with the same metals and ligands we shall now discuss the replacement ability of the different ligands investigated, as well as the conditions essential for studying complexes by paper chromatography.

Several months after the first publications[2,3] on paper chromatography of inorganic ions appeared, ELBEIH, MCOMIE AND POLLARD[4] pointed out that the formation of complexes plays an important role in the separation of metallic ions on filter paper and concluded that for successful chromatographic operation and especially for separation of cations, the formation of complexes is essential. From this time onwards numerous investigations have been published dealing with complex formation and its usefulness for ion separation by paper chromatography. On studying existing publications we found it necessary to divide them into two main categories, dealing with:

(1) Complex formation under "non-homogeneous" and

(2) Complex formation under "homogeneous" conditions.

Non-homogeneous conditions are defined as (a) conditions where metallic complexes or chelates are prepared, then dissolved, and the chromatograms spotted and developed in solvents without the corresponding complexing or chelating agent, as well as (b) conditions where solutions of various metallic salts are spotted and developed in eluting solvents containing a complexing agent. In contrast to these, homogeneous conditions are defined as those conditions where the cationic solutions spotted on the paper are those of the prepared complexes and development is carried out with solvents containing the same complexing agent.

POLLARD, MCOMIE AND ELBEIH[5] developed a systematic procedure for the separation of common cations in dilute mineral acids, based on the different mobilities of the various ions in presence of such complexing agents as benzoylacetone, collidine and antipyrine. They pointed out that it is often preferable to convert the original salt on the paper into the complex whose anion is present in the eluting solution. The authors produced the complexes — *in situ* — by adding the complex-forming agent only to the solvent mixture. Using the same eluting solvent, the authors proved by the cellulose column method that of the four cations, iron, arsenic, copper and cadmium, only iron and copper formed complexes with the complexing agent in the

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TABLE I

R_F VALUES OF CATION-COÖRDINATION COMPOUNDS IN SOLVENT MIXTURES OF *n*-BUTANOL WITH VARIOUS NORMALITIES OF ACETIC ACID

		1N	*2N*	*3N*	*4N*	*6N*
Ce	i	*0.04*	*0.10*	*0.18*	*0.27*	*0.41*
	ii	0.00	0.05	0.08	0.16	0.30
	iii	0.00	0.03	0.08	0.16	0.29
	iv	0.00	0.08	0.09	0.22	0.33
La	i	*0.06*	*0.08*	*0.16*	*0.22*	*0.42*
	ii	0.08	0.08	0.16	0.28	0.45
	iii	0.29t	0.28t	0.38	0.42	0.52
	iv	0.42t	0.44t	0.46t	0.50t	0.59t
Ca	i	*0.08*	*0.12*	*0.21*	*0.32*	*0.49*
	ii	0.14	0.18	0.24	0.32	0.46
	iii	0.46	0.48	0.40	0.45	0.50
	iv	0.55	0.58	0.63	0.65	0.65
Mg	i	*0.08*	*0.14*	*0.23*	*0.30*	*0.50*
	ii	0.18	0.23	0.29	0.39	0.55
	iii	0.52	0.51	0.54	0.59	0.68
	iv	0.73	0.75	0.77	0.73	0.85
Zn	i	*0.24*	*0.28*	*0.35*	*0.42*	*0.52*
	ii	0.32	0.35	0.40	0.44	0.57
	iii	0.58	0.60	0.65	0.67	0.63
	iv	0.72	0.69	0.72	0.79	0.78
Cd	i	*0.19*	*0.28*	*0.37*	*0.42*	*0.52*
	ii	0.30	0.33	0.40	0.43	0.54
	iii	0.59	0.56	0.52	0.53	0.58
	iv	0.73	0.68	0.75	0.72	0.65
Cu	i	*0.23*	*0.27*	*0.36*	*0.41*	*0.49*
	ii	0.30	0.35	0.40	0.45	0.55
	iii	0.53	0.48	0.51	0.51	0.61
	iv	0.77	0.80	0.81	0.80	0.70

eluant. LEDERER[6] found that thiocyanic acid can be used for the separation of the gadolinium group rare earths; no complex formation of ions of the rare earths was found to take place with acetylacetone, tributyl phosphate, ethyl acetoacetate and acetic acid in presence of even dilute hydrochloric acid.

ANDERSON AND MARTIN[7] studied metallic complexes, using as solvent butanol saturated with aqueous solutions of various organic acids and using different metallic salt solutions as spot solutions. The authors consider in several cases that certain metals remain as salts of the anion taken in the original spot solution. The multispot phenomenon, thoroughly reviewed recently by POLLARD, MCOMIE, *et al.*[8], may also serve as an example of complex formation by paper chromatography under non-homogeneous conditions.

CARVALHO[9] and CARVALHO AND LEDERER[10] studied metal chlorides in butanol-hydrochloric acid mixtures under homogeneous conditions. The metal bromides[11], acetates and chloroacetates[1] were studied by spotting solutions of the metal-ligand compounds and developing the chromatograms in solvent mixtures of butanol with the corresponding ligand-acids. Under identical conditions the metal nitrates were studied and R_F values measured[12].

TABLE II

R_F VALUES OF CATION-COÖRDINATION COMPOUNDS IN SOLVENT MIXTURES OF *n*-BUTANOL WITH VARIOUS NORMALITIES OF MONOCHLOROACETIC ACID

		1N	*2N*	*3N*	*4N*	*6N*
	i	0.12	0.11	0.09	0.09	0.08
	ii	*0.12*	*0.11*	*0.09*	*0.09*	*0.08*
Ce	iii	0.12	0.11	0.09	0.09	0.08
	iv	0.12	0.11	0.09	0.09	0.08
	i	0.24	0.19	0.17	0.16	0.18
	ii	*0.21*	*0.18*	*0.14*	*0.15*	*0.15*
La	iii	0.25	0.21	0.19	0.17	0.20
	iv	0.45	0.25	0.26	0.17	0.24
	i	0.16	0.17	0.15	0.14	0.12
	ii	*0.22*	*0.21*	*0.21*	*0.18*	*0.16*
Ca	iii	0.24	0.29	0.24	0.23	0.19
	iv	0.44	0.34	0.34	0.31	0.31
	i	0.29	0.26	0.27	0.23	0.24
	ii	*0.29*	*0.26*	*0.27*	*0.23*	*0.24*
Mg	iii	0.29	0.26	0.27	0.23	0.24
	iv	0.29	0.26	0.27	0.23	0.24
	i	0.24	0.27	0.25	0.26	0.23
	ii	*0.27*	*0.27*	*0.25*	*0.26*	*0.23*
Zn	iii	0.28	0.27	0.25	0.26	0.23
	iv	0.29	0.27	0.25	0.26	0.23
	i	0.37	0.38	0.34	0.32	0.33
	ii	*0.36*	*0.35*	*0.36*	*0.36*	*0.35*
Cd	iii	0.49	0.42	0.39	0.28	0.34
	iv	0.56	0.53	0.46	0.56	0.55
	i	0.39	0.35	0.39	0.33	0.37
	ii	*0.45*	*0.43*	*0.42*	*0.38*	*0.39*
Cu	iii	0.50	0.45	0.43	0.43	0.42
	iv	0.55	0.51	0.49	0.46	0.49

The experiments described below were carried out with the aim of making a comparative study of complex formation under homogeneous and non-homogeneous conditions. The results were also interpreted from the point of view of replacement ability of the ligands investigated.

EXPERIMENTAL*

The method, procedure and technique used in this investigation have been described previously[1]. The same cation initial spot solutions as well as identical butanol–complexing agent solvent mixtures were used. The cations investigated were as before Ce, La, Ca, Mg, Zn, Cd and Cu. The complexant-acids used were acetic, mono-, di- and trichloroacetic acids.

Each cation-acetate (i), -monochloroacetate (ii), -dichloroacetate (iii) and -trichloroacetate (iv) was chromatographed in different normalities of the four complexant acid-butanol solvent mixtures.

RESULTS AND DISCUSSION

Tables I-IV show the R_F values measured. The values printed in italics are those obtained under homogeneous conditions: the ligand in the initial spot solution is

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* This research was undertaken when the author was a guest research worker at the Institut du Radium, Laboratoire Curie, Paris. The author is extremely grateful to Dr. M. LEDERER for his consideration and to Prof. F. JOLIOT and Dr. G. BOUISSIÈRES for permission to work at the Institut.

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TABLE III

R_F VALUES OF CATION-COÖRDINATION COMPOUNDS IN SOLVENT MIXTURES OF *n*-BUTANOL WITH VARIOUS NORMALITIES OF DICHLOROACETIC ACID

		1N	*2N*	*3N*	*4N*	*6N*
Ce	i	0.32 ·	0.21	0.05	0.03	0.90
	ii	0.15	0.10	0.04	0.02	0.90
	iii	*0.14*	*0.10*	*0.04*	*0.02*	*0.90*
	iv	0.15	0.10	0.04	0.02	0.90
La	i	0.36	0.26	0.20	0.12	0.94
	ii	0.26	0.19	0.14	0.08	0.77
	iii	*0.38*	*0.27*	*0.23*	*0.16*	*0.76*
	iv	0.33	0.27	0.20	0.15	0.80
Ca	i	0.30	0.13	0.23	0.08	0.89
	ii	0.39	0.25	0.21	0.19	0.82
	iii	*0.45*	*0.32*	*0.24*	*0.21*	*0.75*
	iv	0.50	0.34	0.26	0.24	0.68
Mg	i	0.41	0.30	0.20	0.12	0.91
	ii	0.44	0.37	0.29	0.22	0.83
	iii	*0.47*	*0.33*	*0.26*	*0.21*	*0.75*
	iv	0.47	0.30	0.23	0.12	0.80
Zn	i	0.47	0.40	0.30	0.23	
	ii	0.48	0.40	0.32	0.24	
	iii	*0.48*	*0.42*	*0.34*	*0.26*	
	iv	0.44	0.34	0.27	0.22	
Cd	i	0.56	0.48	0.44	0.37	0.90
	ii	0.54	0.48	0.44	0.38	0.74
	iii	*0.56*	*0.51*	*0.44*	*0.38*	*0.75*
	iv	0.61	0.54	0.46	0.40	0.75
Cu	i	0.54	0.49	0.41	0.34	0.90
	ii	0.56	0.50	0.43	0.38	0.76
	iii	*0.56*	*0.51*	*0.49*	*0.39*	*0.78*
	iv	0.61	0.55	0.50	0.43	

the same as in the eluant. All other values were obtained under non-homogeneous conditions. In no case did "double-spots" appear. Tailing was obtained only in a few cases (marked t in the tables).

From the results obtained in butanol-acetic acid solvent mixtures (Table I) it can be seen that a given metal gave different R_F values with different ligands. The R_F values increased from cation-i to cation-iv. The differences in the R_F values of a cation with different ligands decreased with increasing concentration of acetic acid in the eluant, but even in 6*N* acid solution the ligand from the eluant cannot completely replace the initial ligand from the spot solution. Monochloroacetic acid as complexant in the eluant (Table II) completely destroys all the initial coördination compounds of cerium, magnesium and zinc already in 1*N* solution. The coördination compounds of other cations investigated seem to be more or less stable; the most stable being those of copper. The acetate compounds are unstable and in most cases are easily replaced by monochloroacetate even in 1*N* solution. The dichloroacetate from the initial solution is replaced only in higher concentrations of monochloroacetic acid in the eluant. A higher replacement ability of the complexing agent in the eluant

TABLE IV

Rf VALUES OF CATION-COÖRDINATION COMPOUNDS IN SOLVENT MIXTURES OF *n*-BUTANOL WITH VARIOUS NORMALITIES OF TRICHLOROACETIC ACID

		1N	*2N*	*3N*	*4N*	*6N*
Ce	i	0.56	0.40			
	ii	0.48	0.33			
	iii	0.44	0.31			
	iv	*0.47*	*0.34*			
La	i	0.64	0.50			
	ii	0.61	0.42			
	iii	0.65	0.43			
	iv	*0.62*	*0.43*			
Ca	i	0.53	0.40			
	ii	0.61	0.50			
	iii	0.61	0.50			
	iv	*0.61*	*0.50*			
Mg	i	0.63	0.58	0.97	0.95	0.85
	ii	0.56	0.55	0.79	0.80	0.87
	iii	0.63	0.58	0.80	0.81	0.87
	iv	*0.64*	*0.53*	*0.82*	*0.81*	*0.82*
Zn	i	0.68	0.59	0.95	0.90	
	ii	0.65	0.56	0.87	0.87	
	iii	0.69	0.59	0.87	0.87	
	iv	*0.69*	*0.56*	*0.87*	*0.85*	
Cd	i	0.73	0.68	0.93	0.93	0.91
	ii	0.70	0.61	0.76	0.71	
	iii	0.69	0.59			
	iv	*0.68*	*0.61*			
Cu	i	0.73	0.62	0.93	0.93	0.93
	ii	0.70	0.62	0.85	0.81	0.72
	iii	0.71	0.65	0.79	0.76	0.73
	iv	*0.73*	*0.65*	*0.76*	*0.75*	*0.73*

is made manifest by the results obtained in butanol mixtures with dichloroacetic acid. Total replacement of the ligand from the initial spot solution by the dichloroacetate takes place practically already at lower concentrations of dichloroacetic acid, except in the case of calcium. A similar conclusion can be drawn from the results shown in Table IV, with trichloroacetic acid as complexant: the compounds migrating on the paper are those of cation trichloroacetates irrespective of the initial ligand in the spot solution.

Studies of such replacement reactions lead to the establishment of relative orders of stability. We can rank the anions investigated with respect to relative ease of replacement by each other, as

$$CH_3COO^- \rightleftarrows CH_2ClCOO^- \rightleftarrows CHCl_2COO^- \rightleftarrows CCl_3COO^-$$

This ligand replacement reaction in paper chromatography tends to go from left to right. At a certain concentration of the complexant acid in the eluant the reactions may reverse their direction and go from right to left. This concentration depends upon

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the complex-forming ability and at the same time upon the dissociation of the complexant acid, as well as on the stability of the coördination compound formed between the cation and the ligand in the spot solution.

In spite of what has been said above, it can be supposed that only in exceptional cases does proper complex formation take place in the presence of an acid in the eluant that is more dissociated than the hydrogen form of the complexant, — or in the presence of an anion in the initial spot solution whose hydrogen form is more dissociated than the hydrogen form of the complexant in the eluant. Therefore, the results obtained with classical solvent mixtures such as organic solvent + complexing agent + mineral acid cannot be interpreted as complex formation in paper chromatography. Indeed, from the results tabulated, it can be seen that for proper interpretation of the results for complexes formed in paper chromatography the conditions considered as homogeneous are essential.

It must be borne in mind that in cases where the rate of exchange of the ligands in complexes is more closely related to bond type than to stability, the above consideration does not apply and results obtained by paper chromatography cannot be compared. In our case replacement reactions with structurally similar ligands were carried out and therefore identical bond type may be supposed between the metal and the different complexing agents investigated.

SUMMARY

In the case of metal complexes the effects of the ligands upon the R_F values obtained in paper chromatography are shown. The replacement ability of the different ligands has been illustrated. Chromatographic studies involving complexes were divided into homogeneous and non-homogeneous types and the experimental results explained accordingly.

RÉSUMÉ

On montre l'effet des groupes organiques sur les valeurs R_F obtenues en chromatographie sur papier dans un composé où un métal est lié par liaison de coordination. La capacité de remplacement des différents groupes est mise en évidence. Les études chromatographiques de complexes sont divisées en deux catégories: type homogène et type non homogène; les conditions ont été définies.

ZUSAMMENFASSUNG

Die Wirkungen der Liganden von Metallkomplexen auf die papier-chromatographisch erhaltenen R_F-Werte werden auseinandergesetzt. Die Ersatzfähigkeit der verschiedenen Liganden wird deutlich gemacht. Die chromatographischen Studien über Komplexe werden in zwei Gruppen eingeteilt, homogene und nicht-homogene Typen, und die Versuchsergebnisse werden dementsprechend ausgelegt.

REFERENCES

[1] A. S. Kertes, *J. chim. phys.*, 54 (1957) 117; *Research* (London), 1957, in the press.
[2] T. V. Arden, F. H. Burstall, G. R. Davies, J. A. Lewis and R. P. Linstead, *Nature*, 162 (1948) 691.
[3] M. Lederer, *Anal. Chim. Acta*, 2 (1948) 261.
[4] I. I. M. Elbeih, J. F. W. McOmie and F. H. Pollard, *Discussions Faraday Soc.*, 7 (1949) 183.
[5] F. H. Pollard, J. F. W. McOmie and I. I. M. Elbeih, *J. Chem. Soc.*, (1951) 466, 470.
[6] M. Lederer, *Anal. Chim. Acta*, 15 (1956) 122.
[7] J. R. A. Anderson and E. C. Martin, *Anal. Chim. Acta*, 13 (1955) 253.
[8] F. H. Pollard, J. F. W. McOmie, J. V. Martin and C. J. Hardy, *J. Chem. Soc.*, (1955) 4332.
[9] R. G. de Carvalho, *Paper presented at the Lisbon Analytical Congress*, Sept., 1956.
[10] R. G. de Carvalho and M. Lederer, *Anal. Chim. Acta*, 13 (1955) 437.
[11] S. Kertes and M. Lederer, *Anal. Chim. Acta*, 15 (1956) 543.
[12] C. Bergamini and A. Rovai, *Anal. Chim. Acta*, 15 (1956) 43.

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ELEKTROPHORESE DER HALOGENOKOMPLEXE VON Hg(II), Bi(III), Cd(II), Pb(II) UND Cu(II)

I. CHLOROKOMPLEXE IN CHLORWASSERSTOFFSÄURE

von

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EINLEITUNG

Michl[1] trennte durch Hochspannungselektrophorese Cu-Cd in 10%-iger Essigsäure. Lederer und Ward[2] gelang die Trennung Hg-Bi-Cd-Pb-Cu durch Niederspannungselektrophorese ($H = 3.9$ V/cm) zwischen Glasplatten in 0.1-0.5*N* HCl. Diese Trennung ist zur Zeit die beste: Hg wanderte 5 cm anodisch, und Cu 4.4 cm kathodisch. Strain[3] versuchte diese Trennung in 0.1*M* Milchsäure. Die vollständige Trennung wurde aber erst nach nachträglicher Behandlung mit Ammoniak und darauffolgender Elektrophorese in der zweiten Richtung erreicht. Werner und Westphal[4] beschrieben eine Trennung von Cd-Pb-Cu durch Hochspannungselektrophorese in 2*N* Essigsäure - 0.6*N* Ameisensäure bei pH ∼ 2. Die Wanderungsdifferenz von Cd-Cu betrug *ca.* 10 cm.

PROBLEMSTELLUNG

Aus den Diagrammen $u = f(c)$, wo u die Beweglichkeit der Metallkomplexe im elektrischen Felde und c die Konzentration des komplexierenden Reagens bedeutet, wurde folgendes unmittelbar ersichtlich:

1. Die Änderung des physikalisch-chemischen Zustandes eines Ions in wässriger Lösung, bewirkt durch die Änderung der Konzentration des ihn umgebenden starken oder schwachen Elektrolyten. Besonders wäre die Beweglichkeit eines fremden Ions in einer möglichst konzentrierten Elektrolytlösung interessant.
2. Die günstigen Bedingungen, bzw. die Auswahl des Trägerelektrolyts und dessen Konzentration, für eine bestimmte Trennung durch Elektromigration, zwecks qualitativer und quantitativer Mikroanalyse, oder einer kontinuierlichen elektrophoretischen Trennung.

Das eben Erörterte ist durch freie Elektrophorese unlösbar, besonders bei Verwendung von konzentrierten starken Elektrolytlösungen mit hoher elektrischer Leitfähigkeit. Wir haben uns für die Trägerelektrophorese bzw. Papierelektrophorese entschlossen, weil durch diese Methodik die Möglichkeit geboten ist, die Joulesche Wärme, auch bei hohen spezifischen Stromleistungen, mit Erfolg abzuführen; ausserdem kann die Papierelektrophorese, wegen verhinderter Konvektion im porösen Träger, auch bei Temperaturen angewendet werden, die etwas höher als die Zimmertemperatur liegen.

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DIE STARKSTROM- UND HOCHSPANNUNGSAPPARATUR

Eine für unsere Zwecke geeignete Apparatur muss unter relativ sehr hohen Stromleistungen bis über 50 Watt für 1 cm Papierstreifenbreite, bzw. mit Stromdichten bis 150 mA/cm, den folgenden Anforderungen genügen:

1. Die Temperatur soll von Versuch zu Versuch möglichst konstant gehalten werden trotz erheblichen Leitfähigkeitsvergrösserungen in der Richtung der wachsenden Konzentrationen des Trägerelektrolyts, bzw. des komplexierenden Reagens.

2. Die Verdunstung vom Papier aus soll vollkommen verhindert werden, weil sich sonst Konzentrationsgradienten, Gradienten der elektrischen Feldstärke und Gradienten der Trägerelektrolytgeschwindigkeit am Filtrierpapierstreifen ausbilden[5–9].

Ausserdem muss die Apparatur auch ebensogut mit hohen Spannungen, bis zu 8 kV, arbeiten können. Zum Unterschied von Niederspannungs- und Hochspannungselektrophorese möchten wir diese Arbeitsweise als Starkstromelektrophorese bezeichnen.

Alle bisher aus der Literatur uns bekannten Apparaturen genügen diesen Anforderungen nicht. Die Apparaturen, die zwischen Glasplatten arbeiten, versagen wegen ungenügender Kühlung und Dichtung. Die Hochspannungsapparaturen nach Werner und Westphal[4], und Wieland und Pfleiderer[10] mit sohlegekühlter Unterlage für das Papier sind höchstens nur für schwache Trägerelektrolyte in den notwendigen hohen Konzentrationen verwendbar; ausserdem besteht noch die Gefahr der Verdunstung. Bei der Hochspannungsapparatur nach Michl[1] besteht zwar keine Gefahr der Verdunstung, doch ist die Kühlung der Papierstreifen ungenügend wegen Mangel

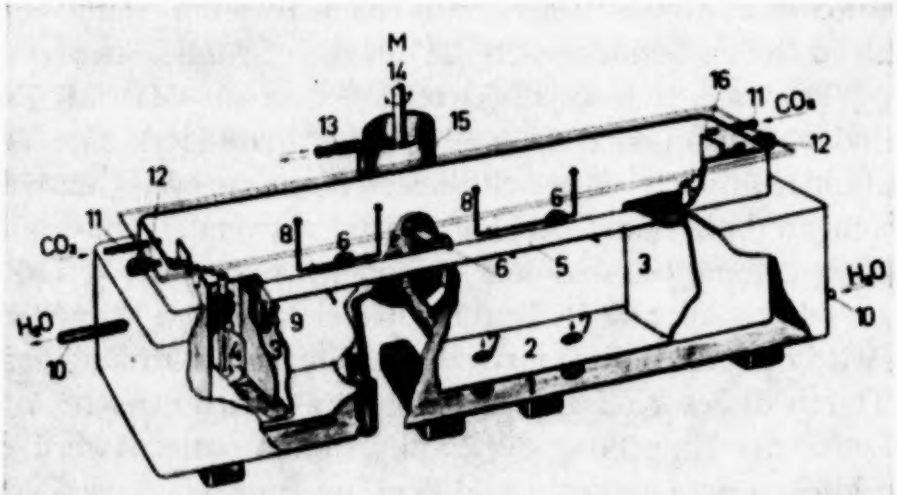

Abb. 1. Schematische Wiedergabe der Apparatur für Starkstrom- und Hochspannungselektrophorese. Baumaterial geschweisstes PVC. Äussere Abmessungen: Länge 100 cm, Höhe 24 cm und Breite 14 cm.

Erklärung der Zeichen: 1. Äusseres Gefäss, 2. Inneres Gefäss, 3. Elektrodenräume mit der Grundelektrolytlösung, 4. Elektrodengefäss aus Glas mit Platindrahtelektroden, 5. Der Filtrierpapierstreifen, 6. Saugöffnungen für das Kühlmittel, 7. Drucköffnungen für das Kühlmittel, 8. Unterstützung des Papierstreifens aus Glas, 9. Gewicht aus Glas zur Spannung des Filtrierpapierstreifens, 10. Zufuhr-, bzw. Abfurrohr für das Kühlwasser, 11. Zufuhr von Kohlendioxyd-Gas, 12. Stromzufuhrbüchse, 13. Füllungs-, bzw. Entleerungsrohr für das Kühlmittel (schweres Benzin), 14. Die Welle der Propellerpumpe für das Kühlmittel, 15. Das Rohr der Propellerpumpe, 16. Der Glasdeckel, M. der Elektromotor für die Propellerpumpe.

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von zwangsläufiger Konvektion und gleichzeitiger Kühlung des Kühlmittels. Wegen vertikaler Aufstellung des Papierstreifens kommt es unbedingt zu starken Flüssigkeitsverschiebungen gegen die untere Elektrode.

Abb. 1. gibt ein Schema der von uns entwickelte und erbaute Apparatur. Die Gesamtansicht von zwei parallellaufenden Apparaturen zeigt Abb. 2. Die äusseren Abmessungen der Apparatur sind: Länge 100 cm, Höhe 24 cm und Breite 14 cm. Das Baumaterial besteht aus sorgfältig geschweissten Polyvinylplatten und Röhre.

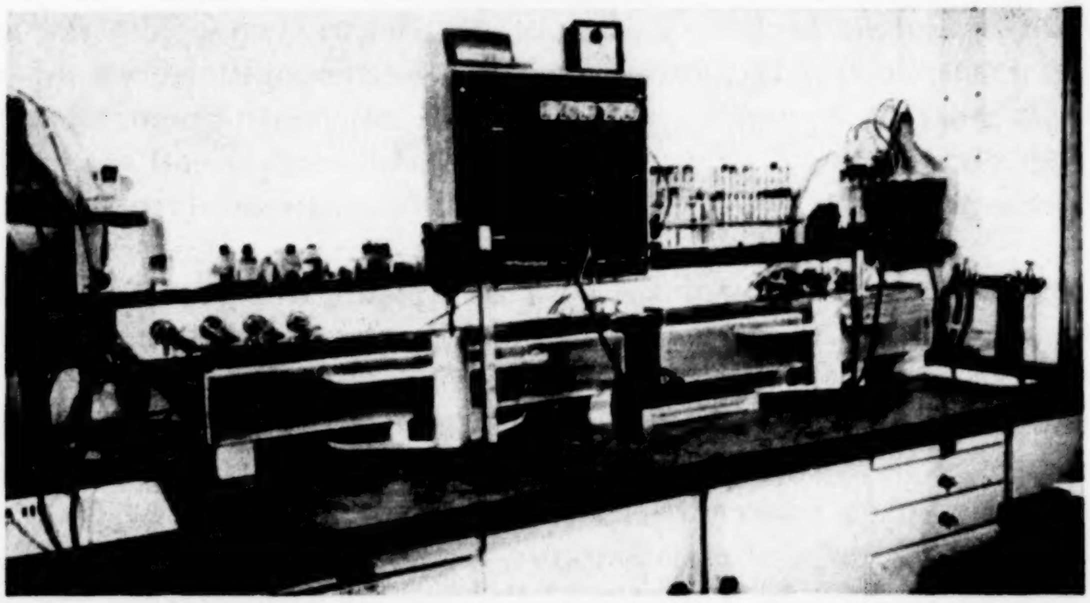

Abb. 2. Die Gesamtansicht der Apparatur für Starkstrom- und Hochspannungselektrophorese.

Die Apparatur besteht im wesentlichen aus einem äusseren (1) und einem inneren (2) Gefäss. Im inneren Gefäss befinden sich die mit dem Grundelektrolyt gefüllten Elektrodenräume (3), in denen sich die Elektrodengefässe aus Glas mit Platindrahtelektroden (4) befinden. Das Filtrierpapier (5), unterstützt durch eine Vorrichtung (8), liegt horizontal im Kühlmittel, das sich seinerseits im inneren Gefäss bis etwas über die Abführöffnungen (6) befindet. Als Kühlmittel verwenden wir durch Vakuumdestillation sorgfältig gereinigtes schweres Benzin („white spirit"). Das Volumen des Kühlmittels ist 15 l pro Apparatur. Durch einen elektrischen Propellerrührer, der als Pumpe wirkt, wird das Kühlmittel fortwährend durch die Öffnungen (7) ein- und (6) ausgepumpt. Durch dieses Kreisen des Kühlmittels wird erreicht, dass das warme Benzin ständig aus der Umgebung der Papierstreifen entfernt wird.

Der Raum zwischen dem äusseren und dem inneren Gefäss wird vom Kühlwasser zwecks Kühlung des Benzins durchströmt. Zur Vermeidung von Feuergefahr wird die Oberfläche des Benzins durch Kohlendioxyd-Gas geschützt. Beim Filtrierpapierwechsel wird das Kühlmittel durch das Entleerungs-, bzw. Füllungsrohr (13) in gesondert auf höheres Niveau aufgestellte Glasvorratsgefässe (Abb. 2) durch das Vakuum gepumpt.

DIE ELEKTROPHORESE IN PORÖSEM ADSORBENS

Bei der Elektrophorese in porösem Adsorbens muss die elektrophoretische Beweglichkeit der Zonen hinsichtlich der Porosität, Adsorption und Elektro-osmose korrigiert werden.

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KUNKEL UND TISELIUS[12] haben für die Korrektion der Beweglichkeiten wegen Struktur und Porosität des Filtrierpapiers den Quotienten L'/L eingeführt. Hier bedeutet L' den wahren, und L den apparenten Weg der Teilchen durch die Struktur des porösen Trägers. Auf leicht übersichtliche Weise ergibt sich für die Korrektion der Beweglichkeit im porösen Träger

$$u = u' \left(\frac{L'}{L}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Hier ist u die wahre Beweglichkeit, und u' die apparente. Wir sind auf einem anderen Wege[7] mit Hilfe des Produkts K_0p zur selben Lösung gekommen, wobei leicht ersichtlich ist dass

$$K_0p = \frac{L'}{L} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

K_0 ist die Widerstandskapazität eines Stücks quadratischen Filtrierpapiers, das bizur Sättigung befeuchtet ist, und die Dimensionen 1 × 1 cm hat. Diese Widerstandsskapazität K_0 ist eine Konstante, die nur von Filtrierpapierqualität und -dicke abhängig ist. Die freie Schichtdicke der Elektrolytlösung am Papier p kann durch Wägen des trockenen und des feuchten Filtrierpapiers ermittelt werden, da $p = q/l$ ist, wo q den freien Querschnitt des Papierstreifens senkrecht zur Stromrichtung, und l die Filtrierpapierstreifenbreite bedeutet. Die freie Schichtdicke p ist von der Temperatur, der Qualität und der Dicke des Filtrierpapiers abhängig. Wir haben experimentell gezeigt[6], dass p praktisch für eine Filtrierpapiersorte bei gegebener Temperatur konstant ist. Für Munktelpapier No. 20/150 wurde p durch Wägung[6] und K_0 mittels $K_0 = H\,l\,\chi\,/I$ ermittelt[7]. H ist die elektrische Feldstärke, l die Papierstreifenbreite, χ die spezifische Leitfähigkeit der Elektrolytlösung mit der der Papierstreifen befeuchtet war und I ist die Stromstärke. Die Resultate waren: $p = 0.036$ cm, $K_0 = 30.4\ \text{cm}^{-1}$, $K_0p = 1.094$ und $K_0^2p^2 \sim 1.2$.

Die Korrektion der Beweglichkeit unter Berücksichtigung von Porosität und Struktur des Munktelpapiers No. 20/150 ergibt sich somit als

$$u = u'K_0^2p^2 \text{ oder } u = 1.2\,u' \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

Der Korrektionsfaktor K_0p is nur von Filtrierpapierqualität und Temperatur abhängig, und unabhängig von der Dicke des verwendeten Filtrierpapiers.

Wenn wir einen eindimensionalen elektrochromatographischen Prozess durch einen diskontinuierlichen zweidimensionalen elektrochromatographischen Prozess in die horizontale (elektrochromatographische) und die vertikale (chromatographische) Komponente auftrennen, ergibt sich die Korrektion der Beweglichkeit einer Zone, die sich in einem Adsorbens bewegt, als[8]

$$u = \frac{1}{R_F}\,u' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

wobei R_F der bekannte chromatographische Faktor ist (hier adsorptionschromatographischer Faktor).

Die apparente elektro-osmotische Beweglichkeit u_e' ist durch Verwendung molekularer Lösungen von ungeladenen Stoffen, wie z.B. Glukose, ermittelbar. Mit Hilfe von (3) und (4) ergibt sich die gesamte Korrektion der elektrophoretischen Beweglichkeit einer Zone, die sich in einem porösen Adsorbens bewegt, als

$$u = 1.2\left(\frac{u'}{R_F} - \frac{u_e'}{R_{F_e}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

wobei R_{F_e} der adsorptionschromatographische Faktor des Stoffes ist, mit dessen Hilfe die apparente elektro-osmotische Beweglichkeit ermittelt wurde.

Die apparente elektrophoretische Beweglichkeit wird bekanntlich durch $u' = s'/H\tau$ ermittelt, wo s' den zurückgelegten apparenten Weg, H die elektrische Feldstärke und τ die Zeit bedeutet. Wir messen den apparenten Weg in Millimetern (mm), die elektrische Feldstärke in Volt pro Zentimeter (V/cm), und die Zeit in Stunden (h). Die Beweglichkeiten haben dann die Dimension [mm V^{-1} h^{-1} cm], und können jederzeit durch Multiplikation mit dem Faktor $0.278 \cdot 10^{-4}$ in die übliche Dimension [$cm^2 V^{-1} sec^{-1}$] übergeführt werden.

EXPERIMENTELLER TEIL

1. Methodische Einzelheiten

Die Filtrierpapierstreifen der Dimension 15 × 700 mm wurden durch die Chlorwasserstoffsäure der zu messenden Konzentration durchgezogen, und zwar so, dass an jedem Ende die Streifen in einer Länge von *ca.* 5—7 cm trocken blieben. Damit wurde eine gleichmässige Befeuchtung der Streifen erreicht. Dann wurden sie, gewöhnlich zu zwei, in die Apparatur montiert (Abb. 1), und mittels Glasgewichte in der richtigen Lage gespannt. Die Elektrodenräume wurden vorher mit der Chlorwasserstoffsäure der zu messenden Konzentration bis zu 1 mm unter den oberen Rand aufgefüllt. Die so montierten Filtrierpapierstreifen hatten eine freie Länge von 660 mm. Jeder Elektrodenraum hatte ein Fassungsvermögen von *ca.* 600 ml. Nach kurzer Zeit wurden auch die unbefeuchteten Reste, an den beiden Enden der Streifen, durch Kapillarkräfte von den beiden Elektrodenräumen aus, gleichmässig mit der Säure befeuchtet. Dann wurde an den Startstrich, der sich stets in der Mitte der Streifen befand, 0.01 ml der Metallsalzlösung mittels einer Mikropipette appliziert.

Die Konzentrationen der Metallsalzlösungen waren 0.1 Grammatom/l, mit Ausnahme von Bi(III) und Pb(II), die wegen Hydrolyse, bzw. kleinerer Löslichkeit der Chloride, in doppelter Verdünnung, d.h. 0.05 Grammatom /l, vorlagen. Die Bi(III)-Lösung wurde ausserdem, wegen Unterdrückung der Hydrolyse, mit HCl angesäuert, sodass die Lösung in bezug auf HCl 0.5*N* war.

Darauf wurde die Apparatur durch initielles Anblasen der Benzinvorratsgefässe mit Benzin bis über die oberen Abführöffnungen selbsttätig durch den Niveauunterschied gefüllt, und der Rest der Apparatur zur Feuersicherung der Benzinoberfläche mit Kohlendioxyd-Gas aufgefüllt. Erst nach dem Einsetzen der Wasserkühlung und der Propellerpumpen wurde der Elektrophoresestrom eingeschaltet.

2. Auswahl der Elektrophoresespannung

Je nach den elektrischen Leitfähigkeiten der Chlorwasserstoffsäurelösungen, bzw. der Papierstreifen, wurde die Spannung so gewählt, dass die Stromleistung pro Apparatur 71 bis 73 Watt betrug. Dafür sind eine maximale Strombelastung von über 250 mA pro Apparatur und eine Stromspannung von 200 bis 3000 V notwendig.

Der Gleichstrom wurde einem im Institut erbauten, ungesiebten Vollweggleichrichter mit kontinuierlicher Spannungsregelung von 100 bis 8000 V und mit einer Ausgangsenergie von 500 Watt in allen Spannungsbereichen entnommen. Die Netzspannung wurde durch einen magnetischen Stabilisator von 2 kVA stabilisiert. Unter diesen Umständen wächst der Strom nur in den ersten 15 Minuten merklich an, und bleibt dann weiter konstant, nachdem die stationäre Temperatur erreicht ist.

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Bei unserer Konstruktion der Elektrodengefässe und Elektrodenräume ist, wegen kleiner Widerstandskapazität, die Spannung an den Papierenden praktisch gleich der Spannung an den Platinelektroden. Die Spannungsdifferenz ist *ca.* 1.5% da die Widerstandskapazität der Elektrodenräume 1.5% der Widerstandskapazität der Filtrierpapierstreifen beträgt. Demzufolge wird die Spannung einfach an den Platinelektroden gemessen. Die Elektrodengefässe sorgen dafür, dass die Produkte der Elektrolyse nicht an die Papierstreifen gelangen können. Die Polarität der Elektroden wurde bei jedem Versuch gewechselt.

3. *Auswahl der Elektrophoresedauer*

Nach unseren Erfahrungen ist es vorteilhaft, bei der Messung elektrophoretischer Beweglichkeiten anorganischer Komplexe in Abhängigkeit von der Konzentration einer starken Säure, die als Komplexbildner fungiert, die Elektrophoresedauer so zu wählen, dass das Produkt $H\tau$ ungefähr 15 [V h cm^{-1}] beträgt. In Ausnahmefällen, namentlich bei sehr grossen Beweglichkeiten der Ionen oder der Komplexe, wird dieses Produkt entsprechend kleiner gewählt (5-10 [V h cm^{-1}]). Durch diese Massnahme werden ausreichend grosse Wegstrecken erreicht, und eine gute Messung derselben ermöglicht. Für die Beweglichkeit selbst ist diese Massnahme belanglos, da sich bei unsereren Experimenten, wie wir uns mehrmals überzeugt haben, die Zonen mit praktisch konstanten Geschwindigkeiten bewegen.

4. *Das Entwickeln und Sichtbarmachen der Zonen*

Nach Beendigung der Elektrophorese und nach dem Ausschalten des Stromes und der Propellerpumpen, wurde das Benzin durch das Vakuum in die Vorratsgefässe zurückgepumpt, die Papierstreifen aus der Apparatur genommen, und spiralenförmig auf Porzellaneinlagen von Vakuumexsikkatoren gelegt. Die Einlagen wurden dann samt den Streifen in die Vakuumexsikkatoren eingelegt, die Luft aus den Exsikkatoren ausgepumpt und Schwefelwasserstoff aus einem Kippschen Apparat kurz eingelassen. Dann wurde durch den im Exsikkator herrschenden Unterdruck über den Vakuumhahn *ca.* 10 ml konzentrierter Ammoniaklösung eingesaugt. Der Vakuumhahn befindet sich am Deckel des Exsikkators, und ist mit einem Glasrohr verbunden, das durch die Mitte bis fast zum Boden des Exsikkators führt. 1-10 Minuten danach sind die Zonen vollkommen entwickelt. Jede Zone kann durch die charakteristische Farbe identifiziert werden: Hg = schwarz, Bi = braun, Cd = gelb, Pb = rötlich-braun, und Cu = grünlich-schwarz. Die Zonen sind *ca.* 14 Tage im trockenen Zustand haltbar.

5. *Resultate*

Abb. 3 gibt die Diagramme der elektrophoretischen Beweglichkeiten der Chlorokomplexe in Chlorwasserstoffsäure von Hg(II), Bi(III), Cd(II), Pb(II) und Cu(II) wieder.

An der Ordinate sind die Beweglichkeiten linear in [mm V^{-1} h^{-1} cm] eingetragen, und zwar so, dass unter positiver Beweglichkeit die Beweglichkeit gegen die Anode, und unter negativer Beweglichkeit die Beweglichkeit gegen die Kathode angenommen wird. Alle Punkte oberhalb der Abszisse sind anionischen Komplexen d.h. Komplexen mit resultierenden negativen Ladungen, und Punkte unterhalb der Abszisse sind kationischen Komplexen, d.h. Komplexen mit resultierenden positiven Ladungen zuzuschreiben. An der Abszisse ist die Konzentration der Chlorwasserstoffsäure im Intervall von 0.1-6*N* linear angegeben.

Gestrichelt sind die apparenten Beweglichkeiten nach der Formel $u' = s'/H\tau$, dagegen sind mit vollen Linien die korrigierten Beweglichkeiten u nach der Gleichung (5) aufgezeichnet. Auf der rechten Ordinate sind die Adsorptions-R_F-Werte angegeben, und ganz oben am Diagramm ist die dazugehörige Adsorption der Metallkomplexe an der Zellulose des Filtrierpapiers durch Adsorptionskurven veranschaulicht. Die mit der Abszissenachse parallele gestrichelte Gerade ,,Eo'' gibt die elektro-osmotische Beweglichkeit wieder, die unabhängig von der HCl-Konzentration war und im ganzen Konzentrationsbereich die Beweglichkeit —0.5 zeigte. Die elektro-osmotische Beweglichkeit wurde mittels Glukose gemessen. Die R_F-Werte der Glukose (Gluk.) waren im ganzen Konzentrationsbereich gleich 1.

Quecksilber ist im ganzen HCl-Konzentrationsbereich anionisch, zeigt aber ein ausgesprochenes Maximum bei 0.7*N* HCl, und besitzt die grösste anionische Beweglichkeit. Wismuth ist ebenso im ganzen Konzentrationsbereich anionisch, mit einem Maximum bei 1.5*N* HCl. Das Abfallen der Beweglichkeit ist aber von da aus langsamer als bei Quecksilber, sodass sich die beiden Kurven bei 2.3*N* HCl kreuzen, bzw. Hg und Bi haben in diesem Punkt dieselbe Beweglichkeit. Weiter von diesem Punkt in der Richtung wachsender HCl-Konzentration hat Bi relativ zu den übrigen Metallen die grösste anionische Beweglichkeit. Zwischen 0.1-0.25*N* HCl ist die Zone von Bi wegen Hydrolyse unscharf (gestrichelte Linie). Kadmium ist von 0.1*N* HCl bis zum isoelektrischen Punkt bei 0.6*N* HCl kationisch, und von diesem Punkt weiter anionisch mit einem Maximum bei 2.3*N* HCl. Blei ist bis 1*N* HCl kationisch, weiter anionisch mit konstanter Beweglichkeit von 3-6*N* HCl. Kupfer ist bis 4.8*N* HCl kationisch und weiter anionisch.

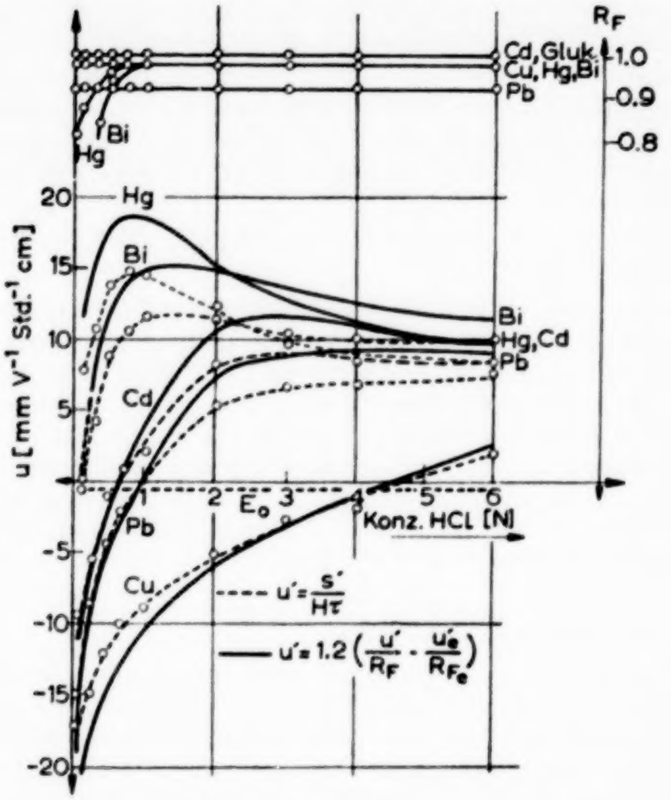

Abb. 3. Die Diagramme der elektrophoretischen Beweglichkeiten der Chlorokomplexe in Chlorwasserstoffsäure von Hg, Bi, Cd, Pb und Cu. Ordinate: die Beweglichkeiten in $[\mathrm{mm\ V^{-1}\ h^{-1}\ cm}]$. Abszisse: HCl-Konzentration von 0.1*N* bis 6*N*. Oberhalb der Abszissenachse wandern alle Ionen anionisch, und unterhalb der Abszissenachse kationisch.

Die apparenten Beweglichkeiten sind gestrichelt, und die nach Gleichung (5) korrigierten Beweglichkeiten sind voll aufgezeichnet. Die Adsorptions R_F-Werte sind auf der rechten Ordinate, und die dazugehörigen Adsorptionskurven der Komplexe an der Zellulose des Filtrierpapiers sind oben im Diagramm ersichtlich.

Filtrierpapier Munktel Nr 20/150, Temperatur 21°C.

6. *Elektrophoretische Trennung eines Gemisches von Hg-Bi-Cd-Pb-Cu in Chlorwasserstoffsäure*

Abb. 4. gibt die Trennung der Metalle Hg-Bi-Cd-Pb-Cu in 1*N* HCl (1), 2*N* HCl (2), und 4*N* HCl (3) wieder.

Der Startstrich ist in der Mitte der Streifen; links war die Anode und rechts die Kathode. Alle Zonen sind vollkommen getrennt. Die Dimensionen der abgebildeten Streifen sind 660 × 15 mm. Bei niedrigen HCl-Konzentrationen wandert die Hg-Zone relativ am schnellsten zu den übrigen

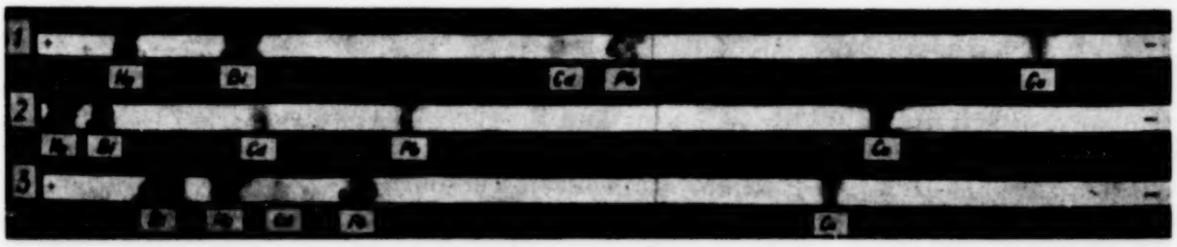

Abb. 4. Die Elektropherogramme der Trennung Hg-Bi-Cd-Pb-Cu in 1*N* HCl (1), 2*N* HCl (2) und 4*N* HCl (3). Startstrich in der Mitte, links Anode, rechts Kathode. Die Dimension der abgebildeten Papierstreifen ist 660 × 15 mm. In 4*N* HCl ist die anodische Beweglichkeit von Bi(III) grösser als die von Hg(II).

Die Elektrophoresedaten:

1. 1*N* HCl, $H = 8.5$ V/cm, $I = 130$ mA/1.5 cm, $\triangle E = 560$ V, $N = 73$ Watt, $t = 21$°C, $\tau = 2.5$ h.
2. 2*N* HCl, $H = 6.97$ V/cm, $I = 155$ mA/1.5 cm, $\triangle E = 460$ V, $N = 71$ Watt, $t = 21$°C, $\tau = 4$ h.
3. 4*N* HCl, $H = 5.6$ V/cm, $I = 192$ mA/1.5 cm, $\triangle E = 370$ V, $N = 71$ Watt, $t = 21$°C, $\tau = 5.75$ h.

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Metallen in der Richtung der Anode. Wie aus dem Diagramm der Beweglichkeiten in Abb. 3 schon zu sehen ist, wandert jedoch Bi in 4*N* HCl am schnellsten.

Die Elektrophoresedauer wurde bei diesen Experimenten so gewählt, dass die Länge der Papierstreifen möglichst gut ausgenützt, und vollkommene Trennung erzielt wurde. Für die weiteren Elektrophoresedaten vergleiche die Erläuterung zu Abb. 4.

SCHLUSSFOLGERUNG UND DISKUSSION

Die Reproduzierbarkeit der Resultate aus Abb. 3 ist ± 5%, was für unsere Problemstellung genügt.

Bei abfallender HCl-Konzentration, namentlich unter 0.1*N*, werden die Resultate unsicher, weil dann die Konzentration des applizierten Metallsalzes dem Grundelektrolyten gegenüber zu gross wird. Ausserdem haben wir in diesem Gebiet eine starke Ausdehnung der Zonen beobachtet. Unserer Ansicht nach müsste man beim Arbeiten in niedrigem Konzentrationsgebiet auch die Konzentration der zu applizierenden Metallsalze stark herabsetzen. Dann werden aber die gewöhnlichen analytischen Methoden der Entwicklung der Zonen unzureichend. Ein Ausweg wäre vielleicht im Übergang zur radioaktiven Tracer-technik zu suchen.

Nach der beschriebenen Arbeitsweise sind die Resultate zwischen 0.1 und 0.5*N* HCl auch noch gelegentlich Störungen unterworfen, obwohl wir strikt Konzentration und Volumen des applizierten Metallsalzes beihalten. Von 0.5*N* HCl aufwärts arbeitet die Methode störungsfrei. Offensichtlich wird die Beweglichkeit bei niedrigen HCl-Konzentrationen durch starke Änderungen von Konzentration und Volumen des applizierten Metallsalzes mehr oder weniger beeinflusst. Diese Beeinflussung soll experimentell in der II. Mitteilung dieser Aufsatzreihe behandelt werden.

Fotos: Aus dem Fotolaboratorium des Institutes „Ruder Bošković".

ZUSAMMENFASSUNG

Es wurde eine Apparatur für Starkstrom- und Hochspannungselektrophorese am Filtrierpapier beschrieben. Diese Apparatur soll Schwierigkeiten umgehen, die sich einer Elektrophorese in starken Grundelektrolyten hoher Konzentration, bzw. grosser elektrischer Leitfähigkeit, widersetzen. Die Zonen wandern über den Papierstreifen mit konstanter Geschwindigkeit, und somit wird die Messung der Beweglichkeiten ermöglicht. Die freie Länge der Filtrierpapierstreifen ist 660 mm. Die Korrektion der apparenten Beweglichkeiten in porösem Adsorbens wurde eingehend behandelt.

Im experimentellen Teil wurden die Diagramme der elektrophoretischen Beweglichkeiten der Chlorokomplexe in Chlorwasserstoffsäure von Hg(II), Bi(III), Cd(II), Pb(II), und Cu(II) wiedergegeben. Die Konzentration der Chlorwasserstoffsäure wurde zwischen 0.1 und 6*N* variiert. In 6*N* HCl liegen alle untersuchten Metalle in anionischen Chlorokomplexen vor. Hg-, Bi-, Cd- und Pb-Chlorokomplexe zeigen im anionischen Bereich ein ausgesprochenes Maximum ihrer Beweglichkeit. Die Reihenfolge der Zonen in der Richtung von der Anode zur Kathode zwischen 0.1 und 2.3*N* HCl ist Hg-Bi-Cd-Pb-Cu, und zwischen 2.3*N* und 6*N* HCl Bi-Hg-Cd-Pb-Cu.

Zum Schluss wurde noch die elektrophoretische Trennung eines Gemisches von Hg-Bi-Cd-Pb-Cu in 1*N* HCl, 2*N* HCl und 4*N* HCl abgebildet. In jedem Experiment wurde eine vollkommene Trennung der Zonen erhalten.

SUMMARY

An apparatus for heavy-current and high-tension electrophoresis on filter paper is described. This apparatus enables one to avoid the difficulties that occur in electrophoresis in base electrolytes that are highly concentrated or show greater electric conductivity. The zones migrate along the paper strips with constant speed and, consequently, it is possible to measure the mobility. The effective length of the filter paper strips is 660 mm. Correction of the apparent mobility in the porous adsorbent is treated thoroughly.

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Diagrams of the electrophoretic mobility of the chloro-complexes of Hg(II), Bi(III), Cd(II), Pb(II), and Cu(II) in hydrochloric acid, are given in the experimental part. The concentration of the hydrochloric acid varied between 0.1*N* and 6*N*. In 6*N* HCl all the metals investigated are present as anionic complexes. Hg, Bi, Cd, and Pb chloro-complexes show a pronounced maximum of mobility in the anionic range. The sequence of the zones in the direction anode to cathode is Hg, Bi, Cd, Pb, Cu at 0.1-2.3*N* HCl and Bi, Hg, Cd, Pb, Cu at 2.3-6*N* HCl.

Finally, the electrophoretic separation of a mixture of Hg, Bi, Cd, Pb, Cu in 1*N*, 2*N* and 4*N* HCl is illustrated. Complete separation of the zones was achieved in each experiment.

RÉSUMÉ

On décrit un appareil pour l'électrophorèse à fort courant et haute tension, sur papier-filtre. Cet appareil permet d'éviter les difficultés qui se présentent lors de l'électrophorèse dans une solution concentrée d'un électrolyte fort et par conséquent d'une grande conductibilité électrique. Les zones recouvrent les bandes du papier avec une vitesse constante, ce qui rend possible la mesure de la mobilité. La longueur utile des bandes du papier-filtre est de 660 mm. On a corrigé l'erreur due à la mobilité apparente dans l'absorbant poreux. Dans la partie expérimentale, on donne les diagrammes des mobilités ,,électrophorétiques" des chlorocomplexes de Hg(II), Bi(III), Cd(II), Pb(II) et Cu(II) en solution chlorhydrique. On a fait varier la concentration de l'acide chlorhydrique entre 0.1 et 6*N*. Dans l'HCl 6*N*, tous les métaux examinés se présentent comme chlorocomplexes anioniques. Les chlorocomplexes de Hg, Bi, Cd et Pb présentent, dans le domaine anionique, un remarquable maximum de mobilité. La succession des zones dans la direction anode-cathode dans l'acide chlorhydrique 0.1 à 2.3*N* est: Hg-Bi-Cd-Pb-Cu et dans HCl 2.3 à 6*N*: Bi-Hg-Cd-Pb-Cu. Enfin, on décrit une séparation par électrophorèse d'un mélange de Hg, Bi, Cd, Pb, Cu dans l'acide chlorhydrique *N*, 2*N* et 4*N*. Dans chaque cas, on obtient une parfaite séparation des zones.

LITERATUR

[1] H. Michl, *Monatsh. Chem.*, 82 (1951) 489.
[2] M. Lederer und F. L. Ward, *Anal. Chim. Acta*, 6 (1952) 355.
[3] H. H. Strain, *Anal. Chem.*, 24 (1952) 356.
[4] G. Werner und O. Westphal, *Angew. Chem.*, 67 (1955) 251.
[5] Z. Pučar, *Arhiv kem.*, 25 (1953) 205.
[6] Z. Pučar, *Arhiv kem.*, 26 (1954) 29.
[7] Z. Pučar, *Arhiv kem.*, 26 (1954) 41.
[8] Z. Pučar, *Croat. Chem. Acta*, 28 (1956) 195.
[9] Z. Pučar, *Croat. Chem. Acta*, 29 (1957) 1.
[10] Th. Wieland und G. Pfleiderer, *Angew. Chem.*, 67 (1955) 257.
[11] Z. Pučar, *Acta Pharm. Jugoslav.*, 4 (1954) 10.
[12] H. G. Kunkel und A. Tiselius, *J. Gen. Physiol.*, 35 (1951) 89.

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ELEKTROPHORESE DER HALOGENOKOMPLEXE VON Hg(II), Bi(III), Cd(II), Pb(II) UND Cu(II)

II. ABHÄNGIGKEIT DER BEWEGLICHKEITEN VON DER KONZENTRATION DES METALLIONS

von

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EINLEITUNG

In einer früheren Mitteilung[1] wurde eine Apparatur für Starkstrom- und Hochspannungselektrophorese beschrieben, und die Anwendbarkeit der Starkstromelektrophorese in der analytischen Chemie, und in der Chemie der Metallkomplexe erörtert.

Im Laufe der Experimente zeigte sich, dass die Beweglichkeiten der Metallkomplexe nicht nur von der Konzentration des Grundelektrolyten, sondern auch noch von der Konzentration des applizierten Metallsalzes abhängig sind.

In der vorliegenden Mitteilung wollen wir die Abhängigkeit der Beweglichkeiten der Chlorokomplexe von Hg(II), Cd(II), Pb(II) und Cu(II) von Konzentration und Volumen der applizierten Metallsalzlösung, und zwar in relativ niedrigen Konzentrationen von Chlorwasserstoffsäure, 0.1*N*, 0.5*N* und 1*N* HCl, experimentell verfolgen.

EXPERIMENTELLER TEIL

1. Änderung der Beweglichkeit mit der Konzentration des Metallions

Wegen experimenteller und methodischer Einzelheiten vergleiche Mitteilung I[1].

Die Fig. 1, 2 und 3 geben die Beweglichkeiten der Chlorokomplexe von Hg(II), Cd(II), Pb(II) und Cu(II) in 0.1*N*, 0.5*N*, bzw. 1*N* HCl in Abhängigkeit von der Konzentration der zu applizierenden Metallsalze wieder. In den vorliegenden Experimenten wurden Metallnitrate und parallel -acetate verwendet. Es konnte kein Unterschied im elektrophoretischen Verhalten der Nitrate und Acetate festgestellt werden. Wismuth wurde wegen Hydrolyse in die vorliegenden Experimente nicht einbezogen.

Die Konzentration der Metallsalze wurde im breiten Intervall von 0.01 (Grammatom/l) bis 1.20 (Grammatom/l) variiert. Das applizierte Volumen war immer 0.01 ml.

Im allgemeinen ist ersichtlich, dass die anionische Beweglichkeit, oberhalb der Abszissenachse, mit wachsender Konzentration des applizierten Metallsalzes abfällt, während sich die kationische Beweglichkeit, unterhalb der Abszissenachse, vergrössert.

Die Änderungen der Beweglichkeiten sind bei 0.1*N* HCl bedeutend, bei 0.5*N* HCl viel kleiner, und bei 1*N* HCl unbedeutend. In 1*N* HCl zeigt nur noch Cu(II) eine deutliche Abhängigkeit der Beweglichkeit von der Konzentration. Kupfer zeigt, infolge nur schwacher Chlorokomplexbildung, die grösste Abhängigkeit der Beweglichkeit von der Konzentration des Metallions. Die Änderungen der Beweglichkeiten in Fig. 1, 2 und 3 sind durch das Massenwirkungsgesetz zu deuten.

Entsprechend der schwächeren Löslichkeit der Hg(II)- und Pb(II)-Salze in HCl, wurde der Konzentrationsbereich, je nach den Verhältnissen, kleiner gewählt.

Kadmium gibt merkwürdigerweise in 0.1*N* und 0.5*N* HCl (Fig. 1 und 2) zwei definierte und getrennte Zonen, von denen die erste Zone beinahe isoelektrisch und kompakt erscheint, während die zweite kationisch und etwas diffuser ist. Bei Konzentrationen des Kadmiums unter 0.2 Grammatom/l verschwindet die erste Zone vollkommen, und es bleibt nur noch die zweite, kationische, Zone übrig. In 1*N* HCl ist im ganzen Konzentrationsbereich von Kadmium nur die erste, jetzt anionische, Zone vorhanden. Solche „Multispots" wurden bereits in der Papierchromatographie von CURRY[2] mit Na_2HPO_4-Lösungen, und von ERDEM[3,4,5] mit Systemen, die Cd^{++} und NH_3 enthalten, und auch bei der Chromatographie von Na_2HAsO_4 beobachtet. Bei Papierelektrophorese

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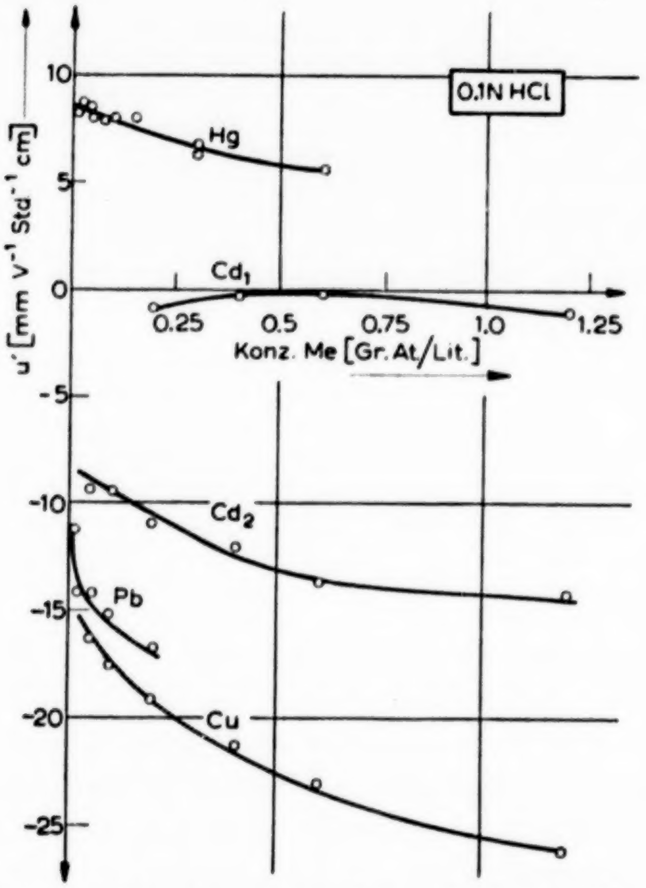

Fig. 1. Die apparenten Beweglichkeiten der Chlorokomplexe in $0.1N$ HCl in Abhängigkeit von der Konzentration der applizierten Metallsalze. Kadmium gibt zwei Zonen („Multispots"). Die Konzentration der applizierten Metallnitrate und Acetate wurde im Interval von 0.01 Grammatom/l bis 1.20 Grammatom/l variiert. Experimentelle Einzelheiten: Methodik: Starkstromelektrophorese am Filtrierpapier; Filtrierpapier: Munktel Nr. 20/150; Dimension der Papierstreifen: 660 × 15 mm; Volumen des applizierten Metallsalzes: 0.01 ml; Stromspannung: $\triangle E = 1850$ V; Elektrische Feldstärke: $H = 28.0$ V/cm; Stromdichte: $I = 39.1$ mA/1.5 cm; Elektrische Leistung: $N = 72$ Watt; Elektrophoresedauer: $\tau = 0.53$ h; Temperatur: $t = 21°$C.

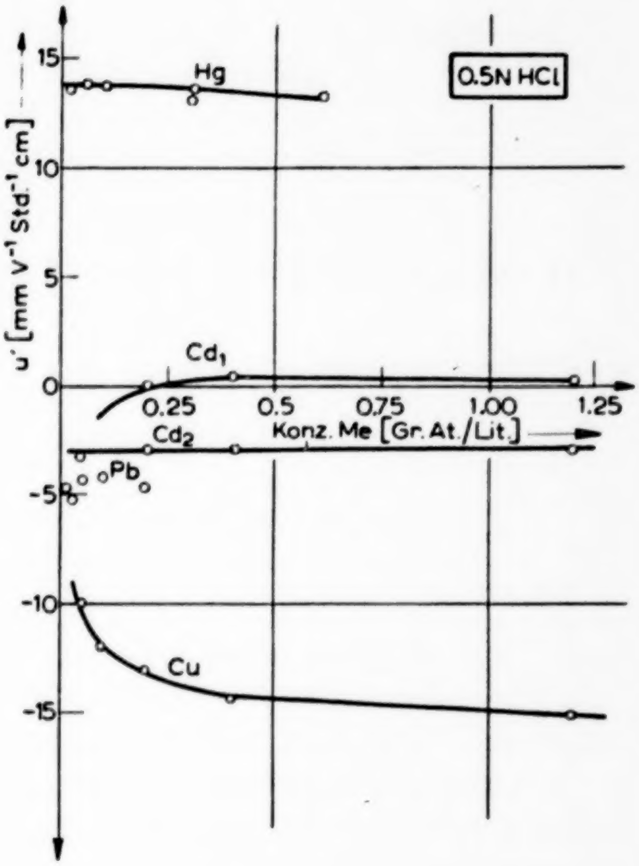

Fig. 2. Die apparenten Beweglichkeiten der Chlorokomplexe in $0.5N$ HCl in Abhängigkeit von der Konzentration der applizierten Metallsalze. Kadmium gibt zwei Zonen („Multispots"). $H = 12.9$ V/cm, $I = 85$ mA/1.5 cm, $\triangle E = 850$ V, $N = 72$ Watt, $t = 21°$C, $\tau = 1$ h. Alles Übrige wie Fig. 1.

haben **Bruninx** u. Mitarb.[6] zwei Zonen von Tantal in gepufferter Oxalatlösung erhalten. Es sei noch erwähnt, dass wir auch bei der Elektrophorese von Bromo- und Jodokomplexen des Kadmiums, besonders aber bei kleineren Konzentrationen des Halogenions und grösseren Konzentrationen des Kadiums, mehrere, sogar auch vier, „Multispots" von Kadmium beobachten konnten.

2. Änderung der Beweglichkeit mit dem Volumen der applizierten Metallsalzlösung

Im folgenden Experiment haben wir das Volumen der applizierten Metallsalzlösung von 0.005 ml bis 0.05 ml variiert. Als Grundelektrolyt wählten wir $0.1N$ HCl, die kleinste Konzentration in unserem Messbereich[1], weil hier die grössten Änderungen der Beweglichkeit zu erwarten sind.

Es wurden zwei parallele Versuchsreihen aufgestellt: eine mit der Konzentration des zu applizierenden Metallions von 0.02 Grammatom/l, und die andere mit der Konzentration von 0.1 Grammatom/l.

Dementsprechend ergaben sich im allgemeinen für jedes untersuchte Metallion zwei Kurven (Fig. 4). Die obere Kurve entspricht der kleineren Konzentration des applizierten Metallions (0.02 Grammatom/l), und die untere der grösseren Konzentration (0.1 Grammatom/l). Wie nach Fig. 1. zu erwarten war, waren die Beweglichkeiten im kationischen Gebiet für kleinere Konzentrationen des Metallions kleiner als die Beweglichkeiten für grössere Konzentrationen des Metallions, und

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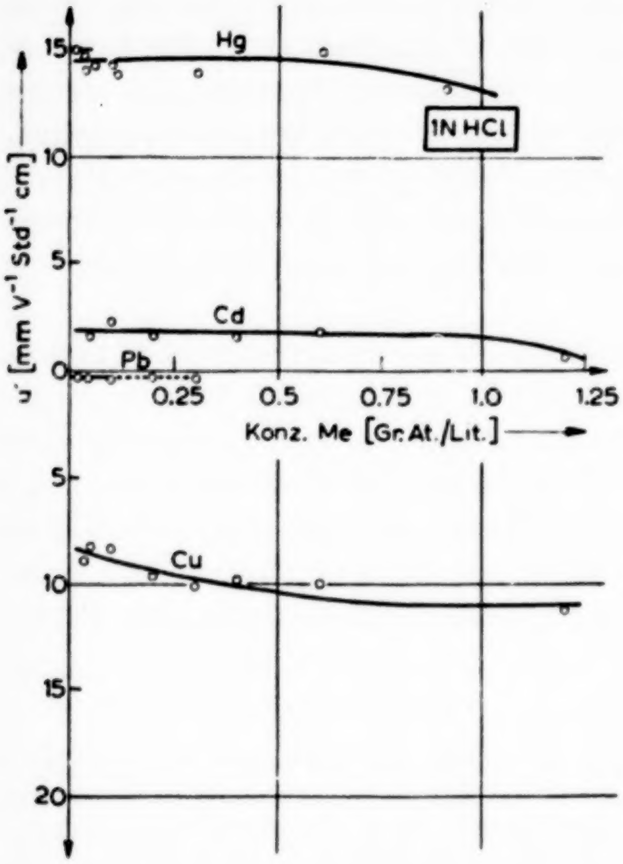

Fig. 3. Die apparenten Beweglichkeiten der Chlorokomplexe in 1 N HCl in Abhängigkeit von der Konzentration der applizierten Metallsalze. Kadmium zeigt keinen ,,Multispot"-Effekt.

$H = 8.65$ V/cm, $I = 126$ mA/1.5 cm, $\Delta E = 570$ V, $N = 72$ Watt, $t = 21$°C, $\tau = 2.1$ h. Alles Übrige wie Fig. 1.

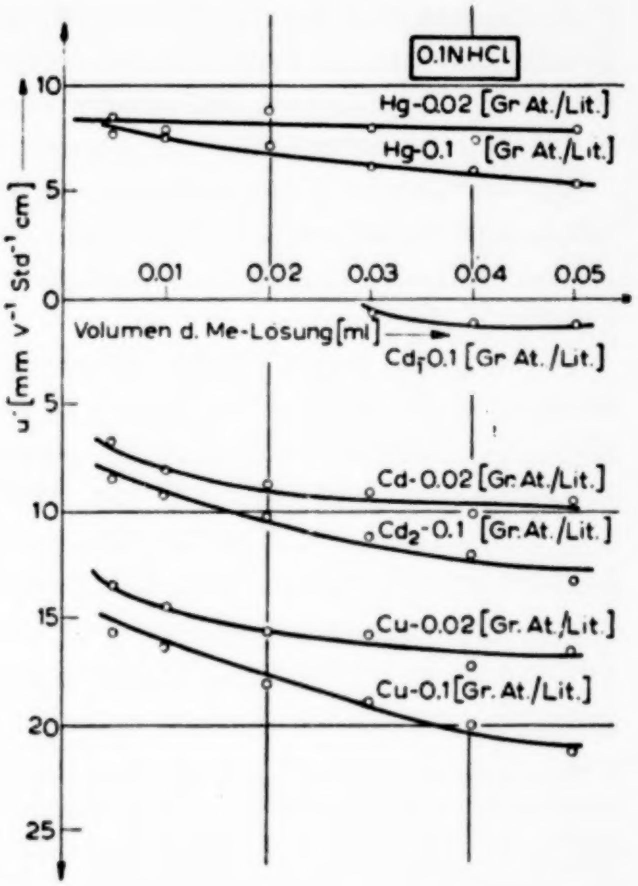

Fig. 4. Die apparenten Beweglichkeiten der Chlorokomplexe in 0.1 N HCl in Abhängigkeit vom applizierten Volumen der Metallnitrate. Das Volumen der applizierten Metallsalzlösungen wurde zwischen 0.005 ml und 0.05 ml variiert.

Es wurden zwei parallele Versuchsreihen aufgestellt: eine mit der Konzentration des applizierten Metallions von 0.02 Grammatom/l, und die andere mit der Konzentration von 0.1 Grammatom/l.

Kadmium zeigte in der Konzentration 0.1 Grammatom/l von 0.03 ml aufwärts den ,,Multispot"-Effekt. Alles Übrige wie Fig. 1.

im anionischen Gebiet umgekehrt. Mit wachsendem Volumen der applizierten Metallsalzlösung fällt die anionische Beweglichkeit ab, während sich die kationische vergrössert.

Kadmium zeigte in kleiner Konzentration (0.02 Grammatom/l) durch den ganzen Bereich des applizierten Volumens keinen ,,Multispot"-Effekt. Dagegen beobachteten wir bei grösserer Konzentration des Kadmiums, namentlich bei 0.1 Grammatom/l, die aus den bereits beschriebenen Experimenten bekannte isoelektrische Zone (Cd_1, Fig. 4), und zwar vom applizierten Volumen (0.03 ml) an aufwärts. Die Beweglichkeit der normalen Zone (Cd_2, Fig. 4), wird durch das Auftreten der isoelektrischen Zone nicht beeinflusst.

SCHLUSSFOLGERUNG UND DISKUSSION

Die Beweglichkeiten der Zonen der Metallkomplexe sind nicht nur abhängig von der Konzentration des Grundelektrolyten (Komplexbildners), sondern auch von Konzentration und Menge des applizierten Metallsalzes, was besonders deutlich zum Vorschein kommt bei kleineren Konzentrationen des Grundelektrolyten. Bei grösserer Konzentration des Grundelektrolyten (1 N und mehr) ist die Abhängigkeit der Beweglichkeiten der Zonen von Menge und Konzentration des applizierten Metallsalzes klein.

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Aus diesen Gründen ist es sehr empfehlenswert, bei systematischen Messungen der Beweglichkeiten als Funktion der Konzentration des Grundelektrolyten die Konzentration des applizierten Metallsalzes wie auch dessen Volumen, besonders im Gebiet niedriger Konzentrationen des Grundelektrolyten, jeweils strikt konstant zu halten.

Mit wachsender Konzentration und Menge, bzw. Volumen, des applizierten Metallsalzes wird die kationische Beweglichkeit der Zonen grösser, und die anionische Beweglichkeit kleiner. Alles bereits Gesagte steht im Einklang mit dem Massenwirkungsgesetz.

Die Neigung einiger Metalle, während der Elektrophorese mehrere Zonen zu bilden, deutet auf die Möglichkeit hin, dass unter besonderen Bedingungen mehrere Komplexe, die nicht im dynamischen Gleichgewicht miteinander stehen, gleichzeitig existenzfähig sind. Das Auftreten von ,,Multispots'' wird durch kleine Konzentration des Grundelektrolyten und grosse Konzentration und Menge des applizierten Metallions begünstigt. Wir haben diese Erscheinung nicht nur an Chloro-, Bromo- und Jodokomplexen des Kadmiums, sondern auch an einigen anderen Metallkomplexen gelegentlich durch Elektrophorese beobachtet.

ZUSAMMENFASSUNG

Es wurde die Abhängigkeit der Beweglichkeiten der Chlorokomplexe von Hg(II), Cd(II), Pb(II) und Cu(II) von Konzentration und Volumen der applizierten Metallsalzlösungen, und zwar in relativ niedrigen Konzentrationen von Chlorwasserstoffsäure ($0.1N$, $0.5N$ und $1N$ HCl), experimentell untersucht. Diese Abhängigkeit ist bei niedrigen Konzentrationen des Grundelektrolyten, unter $1N$ HCl, bedeutend, und bei grösseren Konzentrationen, von $1N$ HCl aufwärts, unbedeutend.

Mit wachsender Konzentration und wachsendem Volumen des applizierten Metallsalzes wird die kationische Beweglichkeit der Zonen grösser, und die anionische Beweglichkeit kleiner.

Unter bestimmten Bedingungen zeigten Chloro-, Bromo-, und Jodokomplexe des Kadmiums mehrere elektrophoretische Zonen (,,Multispots''). Wir haben ,,Multispots'' gelegentlich auch bei der Elektrophorese anderer Metallkomplexe beobachtet.

SUMMARY

The dependence was investigated of the mobilities of the chloro-complexes of Hg(II), Cd(II), Pb(II) and Cu(II) on the concentration and the volume of the metal salt solution applied, the experiments being carried out in relatively low concentrations of hydrochloric acid ($0.1N$, $0.5N$ and $1N$). This dependence is considerable in base electrolytes of low concentration (less than $1N$ HCl) and insignificant in the case of higher concentrations (greater than $1N$ HCl).

On increasing the concentration and volume of the metal salt applied, the cationic mobility of the zones increases and the anionic mobility decreases.

Under certain conditions chloro-, bromo-, and iodo-complexes of cadmium showed multispots. We have occasionally observed these multispots also in the electrophoresis of other metal complexes.

RÉSUMÉ

On a étudié expérimentalement le rapport des mobilités des chlorocomplexes de Hg(II), Cd(II), Pb(II) et Cu(II) avec la concentration et le volume des solutions de sels métalliques utilisées et cela pour des concentrations relativement faibles d'acide chlorhydrique (HCl $N/10$, $N/2$ et N). Ce rapport existe aux faibles concentrations de l'électrolyte de base (inférieures à HCl N). Il est insignifiant aux plus fortes concentrations (supérieures à HCl N).

Quand on augmente la concentration et le volume du sel métallique envisagé, la mobilité ,,cationique'' des zones devient plus grande, tandis que la mobilité ,,anionique'' devient moindre.

Dans des conditions données, les chloro-, bromo- et iodocomplexes du cadmium montrent plusieurs zones d'électrophorèse (,,multispots''). Nous avons d'ailleurs observé des ,,multispots'' lors de l'électrophorèse d'autres complexes métalliques.

LITERATUR

[1] Z. Pučar, *Anal. Chim. Acta*, 17 (1957) 476.
[2] A. S. Curry, *Nature*, 171 (1953) 1026.
[3] B. Erdem und H. Erlenmeyer, *Helv. Chim. Acta*, 37 (1954) 2220.
[4] B. Erdem, *Rev. fac. sci. univ. Istanbul, Sér. C*, 20 (1955) 332.
[5] B. Erdem, *Rev. fac. sci. univ. Istanbul, Sér. C*, 20 (1955) 36.
[6] E. Bruninx, J. Eeckhout und J. Gillis, *Anal. Chim. Acta*, 14 (1956) 74.

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ELECTRO-STATIC DISCHARGE METHOD OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

PART I

by

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The method described in this paper is entirely new. Use is made of a static-discharge current. The underlying principle can be readily understood by reference to Fig. 1.

If the outer surface on the top of an electric light bulb is coated with a conducting layer L and the latter is connected to a gold leaf (or other) electroscope, the latter attains a static charge equal to the peak voltage of the electric light mains from which the filament is heated. This can be decreased by the insertion of a variable resistance R.

The peak voltage is steadily maintained for as long as the electron supply from the lamp is as great as are the losses due to leakage. If the leakage exceeds the supply, the voltage indicated by the electroscope will show a corresponding reduction, *e.g.*

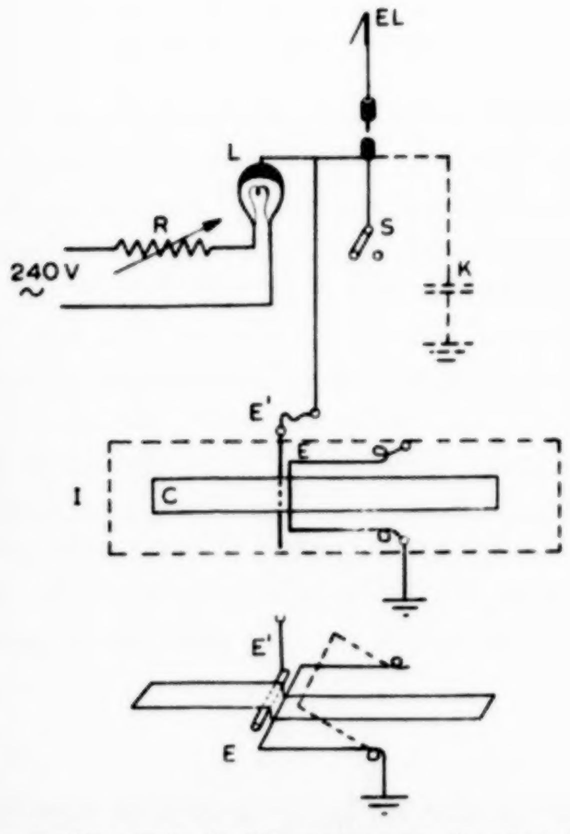

Fig. 1. BLAKE's electro-static zone locater, fed from an electric light bulb. The sketch below shows the arrangement for inserting a chromatograph by lifting the spring electrode E. Electroscope or neon detection may be employed.

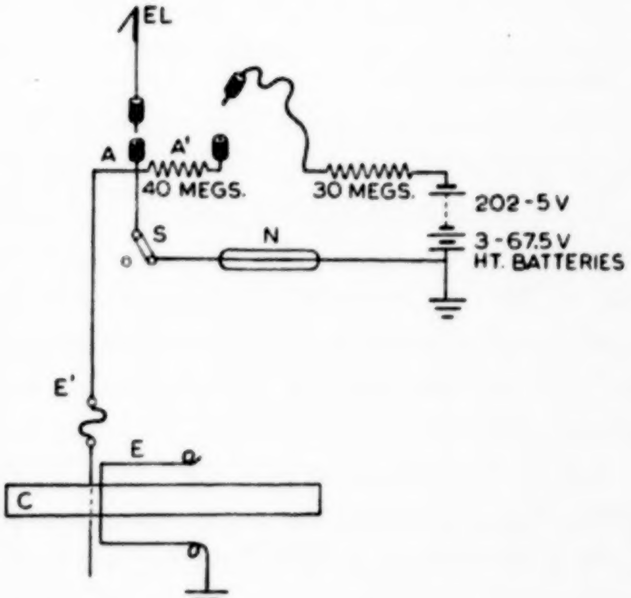

Fig. 2. The neon tube in this figure is fed from batteries instead of from the lamp.

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if a piece of filter paper is held against the electroscope its leaf will fall to, say, about two-thirds of its peak position. However, the leaf will collapse to zero when touched by a paper that has previously been impregnated with a small quantity of even a weak solution of any conductive solute. Again, if the electroscope be touched by hand, its potential will fall to zero and will recover its original voltage as soon as the hand is removed.

It is but one short step from this to the application of static discharge currents for the location of chromatograph zones or spots. The dotted lines I (Fig. 1.) indicate a strip of polystyrene or other insulating material on which are mounted two electrodes made of stiff springy nickel-plated bronze wire (about No. 16 B.W.G.). Electrode E′ is a fixture and is connected to the electroscope. The other electrode E is earthed. This can be lifted as indicated by dotted lines in order that a chromatograph C may be inserted beneath it. When the latter is moved over the top of E′ and underneath E, as each zone or spot bridges the space which separates the electrodes its presence is immediately detected by movement of the gold leaf.

Should it be found necessary, the capacitance of the electroscope can be increased by connecting a small condenser K having a capacity of the order of, say, 0.0005 μF between it and earth.

Neon-tube indicator

A neon tube may be employed in lieu of the electroscope. Connection to the source of electron supply is made first by means of switch S. It will be observed that the clean paper portions of the chromatograph provide sufficient insulation and the neon tube glows; but as soon as a conductive zone bridges the gap, the potential falls below the threshold voltage of the tube, the glow ceases and does not appear again until the other edge of the zone has crossed the gap.

Valve electroscope

G. G. BLAKE's valve electroscope[2], E. B. MOULLIN's thermionic volt meter[3], or the simplified thermionic volt meter of T. B. RYMER[4], may be employed in place of a gold leaf electroscope to register the voltage variations in terms of current change thus making possible the employment of a current-operated recording instrument. The writer has made some quite satisfactory preliminary tests in this direction.

Although the neon-tube method had the merit of being very simple and may be used for certain specific purposes the writer recommends the electroscope method for general use.

A gold leaf electroscope will record either voltage decrease or increase, in accordance with either more or less conductance of the zone or spot. These are measurable if the electroscope is fitted with a scale. Higher voltage is required in the latter case.

MATHAL[1], who discovered this method of charging an electroscope, silvered the top of his electric light bulb, but the writer has found that a coat of aluminium paint answers equally well.

Static charge and discharge from batteries

Instead of obtaining the static charge from an electric lamp it can be supplied from a high tension battery. The writer's scheme (illustrated in Fig. 2), which operates well, provides a very inexpensive portable zone locater.

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QUANTITATIVE DETERMINATIONS

For quantitative measurement of zone content the writer employs the following procedure. After each zone has been located, it is cut out with scissors and its content is dissolved in a measured quantity of distilled water or other solvent. A sample of this solution is then measured in BLAKE's titrimeter[5,6] and the micro-ammeter reading is noted. Small measured quantities of the same solute (taken from stock) are then added successively to a similar quantity of the same solvent and are tested in the titrimeter. When the micro-ammeter reading of the latter agrees with that originally obtained for the dissolved zone, the quantity of solute in each of the solutions must be the same per unit volume.

While new applications for static discharge currents may find many and various uses, the writer does not expect that this new method will replace his R.Rf. impedance method entirely[5,6]. J. BROOMHEAD[7] has shown that the latter can be relied upon to provide quantitative measurements of amounts of the order of 1 mg of each of the alkali metals with an accuracy of 1%, and will detect quantities as small as 10^{-8} g.

SUMMARY

This paper presents an entirely new application of static discharge current for the localization of zones or spots on paper chromatographs. Electroscope and neon-tube methods of location are described. Both methods can be carried out by the same instrument, which is inexpensive to construct, takes up little space, and is portable. Used in conjunction with BLAKE's titrimeter quantitative measurements are made.

RÉSUMÉ

Ce papier présente une application entièrement nouvelle du courant de décharge statique pour la localisation de zones ou de ,,spots'' sur les chromatogrammes. On y décrit une méthode à l'électroscope et une au tube à néon.

Toutes deux utilisent le même instrument qui est peu coûteux, transportable et prend peu de place. Il a été utilisé conjointement avec le titrimètre de BLAKE pour faire des mesures quantitatives.

ZUSAMMENFASSUNG

In dieser Arbeit wird eine ganz neue Anwendung des Entlandungsstromes einer statischen Ladung zur Lokalisierung von Zonen und Flecken auf Papierchromatogrammen beschrieben. Eine elektroskopische und eine Neonröhren-Methode werden beschrieben. Für beide Methoden kann dasselbe Instrument dienen, das billig herzustellen ist, wenig Platz einnimmt und tragbar ist. Es wurde zusammen mit dem Titrimeter des Verfassers zu quantitativen Messungen verwendet.

REFERENCES

[1] A. O. MATHAL, *J. Sci. Instr.*, 29 (1952).
[2] G. G. BLAKE, *Wireless World & Radio Rev.*, 14 (1924) 316.
[3] E. B. MOULLIN, *J. Inst. Elec. Engrs. (London)*, 61 (1922) 295.
[4] T. B. RYMER, *J. Sci. Instr.*, 18 (1941) 166.
[5] G. G. BLAKE, *Conductimetric Analysis at Radio-frequency*, Chapman & Hall, London, 1950.
[6] G. G. BLAKE, *Anal. Chim. Acta*, 16 (1957) 238.
[7] J. BROOMHEAD, *Chem. & Ind. (London)*, (1956) 1474.

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ELECTRO-STATIC DISCHARGE METHOD OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

PART II

by

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In the first part of this paper[1], the writer described an entirely new method for the location and measurement of chromatograph zones or spots by the passage of electro-static discharge currents through the zones. A condenser was first charged to a known potential and the supply of electrons was then maintained at a steady rate. The voltage of the charge was shown to vary in proportion to the electrical resistance of each zone as the chromatograph was passed across the gap between two electrodes connected respectively to the condenser and earth.

It was demonstrated that the required static charge could be obtained from batteries, or from the heated filament of an electric light bulb, and that instead of measuring the voltage variations by means of an electroscope or electrometer they could be evaluated as plate current variations by a valve volt-meter. The present paper presents yet another way in which the steady charging current can be obtained from the heated filament of a thermionic valve, obviating the need for any external source of electron supply.

Further consideration shows that in the triode and other forms of thermionic valve we have all the conditions we require both to supply and maintain the required steady

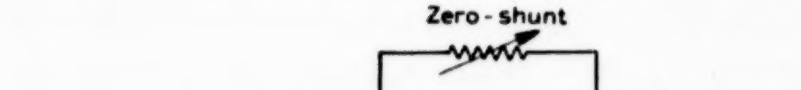

Fig. 1. BLAKE's electro-static discharge method of zone location. Note that the chromatograph takes the place of the usual grid-leak in a zero-shunted triode amplification circuit.

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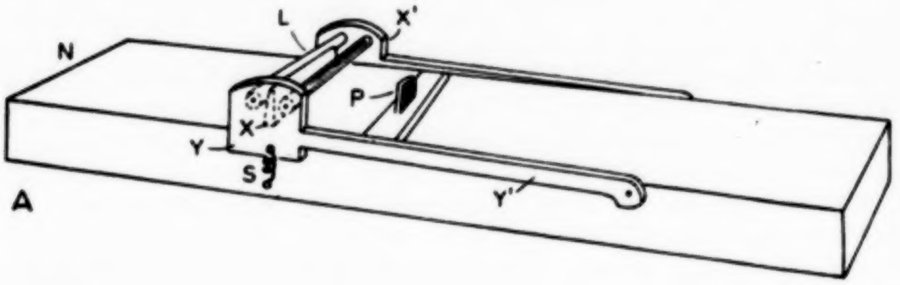
[1] G. G. BLAKE, *Anal. Chim. Acta*, 17 (1957) 489.

electronic charge, in fact we only have to insert the chromatograph between two electrodes respectively to grid and to earth in place of the usual grid-leak. Fig. 1 is a diagram of the circuit which is self-explanatory. Ch indicates the chromatograph in position between the two electrodes X and X′.



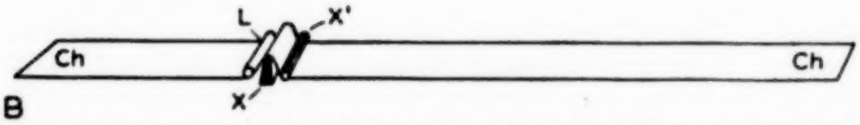


Fig. 2A. This figure shows the position of the electrodes when they are pressed down by means of 2 small springs S one on each side of the insulating platform N of the zone locater.

Fig. 2B. Indicates the position of a chromatograph which lies under the rod L (of insulating material) over the active electrode X and under the earthed electrode **X′**.

Fig. 2 shows the zone locater to which the valve circuit in Fig. 1 is attached. In addition to the two nickel plated electrodes X and X′ there is a rod of insulating material L. Both L and X′ are attached to a hinged metal frame YY′ and can be lifted well above the electrode X while the chromatograph is placed in position. For this purpose a handle P is provided. After the chromatograph has been placed over the active electrode X, 2 small springs (only one of which is shown in the figure at S) hold the frame down in the position required in such a way as to form the chromatograph into a loop as indicated in Fig. 2B. N is an insulating platform across which electrode X is firmly mounted and to which the side pieces of the frame are hinged.

Quantitative determinations

The same method is adopted as that already described in Part I.

SUMMARY

This paper points out that a thermionic valve possesses all the characteristics necessary both to supply and to maintain the steady charging current required for this new method of zone location. The circuit is given for a valve locater and its design is illustrated.

RÉSUMÉ

Cet article signale qu'une valve thermoionique possède tous les caractères nécessaires à la fois pour créer er pour maintenir le charge fixe exigée pour cette nouvelle méthode de localisation des zones. On donne le circuit pour une valve de localisation, accompagné d'un dessin du localiseur de zones.

ZUSAMMENFASSUNG

In dieser Arbeit wird dargelegt dass eine Elektronenröhre alle notwendigen charakteristischen Eigenschaften besitzt um den regelmässigen Ladungsstrom zu liefern und aufrecht zu erhalten, den die neue Zonen-Lokalisierungsmethode erfordert. Stromkreis und Bau des Elektronenröhren-Lokalisators werden mitgeteilt.

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ION EXCHANGE SEPARATION IN THE ANALYSIS OF BISMUTH BASE ALLOYS

PART II. TERNARY ALLOYS CONTAINING URANIUM AND THORIUM

by

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INTRODUCTION

The suitability of anion-exchange procedures for the separation of bismuth in the analysis of bismuth base alloys has been shown for bismuth-uranium and bismuth-thorium binary alloys containing from 50 p.p.m. to 10% of uranium and from 0.05 to 10% of thorium respectively[1]. The procedures are based on the passage of a solution of the sample in molar hydrochloric acid through a column of Deacidite FF in the chloride form; the bismuth is retained by the column whilst the uranium and thorium pass through quantitatively in the acid solution. After the removal of organic matter from solution by wet oxidation, the larger amounts of uranium and thorium are determined volumetrically and the smaller amounts by absorptiometric methods. This investigation has now been extended to the analysis of ternary bismuth base alloys covering compositions from 0.1 to 10% of uranium and thorium respectively. Details of a simple ion exchange method for the separation of the sample into its individual constituents before the final determination of the thorium and uranium are given in this paper.

EXPERIMENTAL

In the initial work the analysis of synthetic ternary alloys was carried out using the same procedures developed for the binary alloys. Although satisfactory results were obtained for some alloys, difficulty was experienced in the analysis of samples with high uranium to thorium ratios. Poor end points were produced in the EDTA titration of thorium in the presence of a ten fold excess of uranium and for these alloys the further separation of the thorium and uranium was necessary. This separation could be effected by introducing a further ion-exchange process based on the fact that thorium is not absorbed by Deacidite FF from 0.05 to 10M hydrochloric acid solution whereas uranium is strongly absorbed from concentrated acid solutions[2]. A suitable procedure for this analysis therefore consisted of two ion-exchange separations according to the following brief outline. After dissolution of a suitable sample weight (about 0.5 g) in nitric acid, the resulting solution is evaporated down several times with hydrochloric acid to remove nitrate ions from solution. The residue is then dissolved in 50 ml of 10% v/v hydrochloric acid and the ion-exchange procedure for the separation of bismuth carried out. The effluent is collected in a 250 ml beaker and then evaporated to fumes of perchloric acid after the addition of 1 ml of this acid (60%). Most of the perchloric acid is removed by heating and the salts dissolved in 10 ml of 9M hydrochloric acid. For the separation of thorium and uranium, this solution is transferred to a small column (5 in. in length and 5 mm in diameter) prepared from 1 g of Deacidite FF and allowed to pass through at a rate of 0.3 ml per minute. The column is washed first with two separate 2 ml aliquots of 9M hydrochloric acid and then with 10 ml of (1 + 1) hydrochloric acid. The thorium is contained in the effluent which is collected in a 125 ml conical beaker. After the addition of about 5 ml of perchloric acid (60%), this solution is evaporated to fumes of perchloric acid and organic matter is destroyed by the addition of concentrated nitric acid. The thorium content is then finally determined either volumetrically with EDTA or absorptiometrically using the coloured thoronol complex. The uranium is recovered from the column in 20 ml of 0.2*M* hydrochloric acid and organic matter in this solution is removed by wet oxidation before proceeding with the uranium determination. Typical results by this procedure for the analysis of three separate synthetic alloy solutions containing 10% uranium and 1.01% thorium were 9.94, 10.0 and 9.98% for uranium and 1.02, 1.015 and 1.02% for thorium respectively. The complete procedure, however, proved very time-consuming and a more rapid procedure which could be applied directly to alloys of all compositions was required. A single ion-exchange procedure for the separation of the sample constituents would meet the requirements and such a procedure would appear to be feasible from the behaviour of bismuth, uranium and thorium in hydrochloric acid solutions with Deacidite FF. Since thorium is not retained by the resin from 0.05 to 10*M* hydrochloric acid solutions, the main problem involved the correct choice of acidity to retain bismuth and uranium on the resin column in the separation of the thorium. Then the uranium could be recovered by the passage of weaker hydrochloric acid through the column.

In the preliminary experiments the behaviour of bismuth in the ion-exchange procedure was studied in more detail and the experiments were designed to obtain the maximum amount of information over a wide range of acid concentrations. Several 500 mg amounts of bismuth metal were dissolved in nitric acid and then changed to chloride media by evaporation in the presence of hydrochloric acid. Each residue was dissolved in 10 ml of the required hydrochloric acid solution and the solution then passed through a column prepared from 8 g of Deacidite FF in the chloride form. Each column was washed with ten 10 ml portions of the requisite strength of acid, but the solutions were collected such that the first 5 washes were separated from the second 5 washes. All solutions were evaporated to fumes of perchloric acid and the bismuth content determined by titration at pH 1.5 with EDTA using pyrocatechol violet as the indicator. The amounts of bismuth passing through columns of Deacidite FF varied considerably with the acidity as shown by the results in Table I.

TABLE I

BEHAVIOUR OF BISMUTH IN THE ION-EXCHANGE SEPARATION

Normality of hydrochloric acid	*Amount of bismuth (mg) passing through column*	
	First 5 washes	*Second 5 washes*
1*N*	not detected	not detected
3*N*	< 0.01	about 0.02
5*N*	< 0.01	about 0.02
7*N*	5.6	47.9
9*N*	28.8	85.8

From the results in Table I solutions with acidities greater than 5*N* cannot be used otherwise the thorium fraction becomes contaminated with bismuth which also complexes with EDTA in the titration procedure for thorium. Solutions of the highest possible acidity must be used, however, to obtain the retention of the uranium on the column. Experiments were therefore carried out to study the recovery of the uranium from bismuth-uranium mixtures containing 500 mg amounts of bismuth and various amounts of uranium in 5*N* hydrochloric acid. After transference of the 10 ml of sample solution to the resin column, the column was washed with five 10 ml portions of 5*N* hydrochloric acid to represent the technique necessary for the recovery of thorium in the analysis of ternary alloys. Then the uranium was removed from the column in five 10 ml portions of 0.2*M* hydrochloric acid, this solution being collected in a 250 ml conical beaker. After the removal of organic matter from the solution by wet oxidation, the uranium content was determined volumetrically with ceric sulphate after reduction to the tetravalent state with a lead reductor. The following good recoveries were obtained for two levels of uranium:

Uranium taken (mg)	49.8	49.8	24.95	24.95
Uranium recovered (mg)	49.5	49.7	24.90	24.95
Error (%)	—0.6	—0.2	—0.2	nil

Although the above results indicated a slight negative bias in this method for uranium, the maximum error was only 0.6% and, moreover, there was no indication of the presence of bismuth in the uranium fraction. Based on this satisfactory behaviour, the following methods were developed for the analysis of ternary alloys. A polarographic method was favoured in this work for the determination of small amounts of uranium. Full details of the methods are as follows:

Methods for the determination of thorium and uranium in bismuth alloys

Special apparatus required

Lead reductor. Take a 10 ml burette, fill it with 10% v/v hydrochloric acid and lightly tamp down a wad of glass wool. Take a quantity of lead, 40 to 60 mesh, and wash it with 50% v/v hydrochloric acid. Then wash the lead with 10% v/v hydrochloric acid and stir it to break up the caked material before pouring into the burette. Allow the lead to settle under its own weight until a column of about 6 inches is formed in the burette. Before use, wash the column with 10 ml of 25% v/v hydrochloric acid containing a little ferric iron, followed by 20 to 25 ml of 10% v/v hydrochloric acid.

Reagents required

Deacidite FF. Dry the commercially supplied product at about 40°C and grind it to pass a B.S. 40 mesh sieve. Stir with water and allow to settle for 2 to 3 minutes, before pouring off the supernate and 'fines'. Repeat this 2 or 3 times. Stir the resin successively with 50% v/v hydrochloric acid, water, cold 10% w/v sodium hydroxide, water, *N* nitric acid, 10% v/v hydrochloric acid and water. Dry at about 40°C in a tray and store in a bottle until required.

0.02M EDTA. Dissolve 7.45 g of the disodium salt of ethylenediaminetetraacetic acid in 1 l of distilled water and standardise against a standard zinc solution using Eriochrome Black T as the indicator.

0.02N ceric sulphate. Dissolve 11 g of A.R. $Ce(NO_3)_4 \cdot 2NH_4NO_3$ in 1 l of *N* sulphuric acid. Determine the strength of this solution by titration against ferrous ammonium sulphate which has been standardised against potassium dichromate. Store the solution in a dark glass bottle.

0.1% pyrocatechol violet. Dissolve 100 mg of the reagent in 100 ml of distilled water.

0.001N ferroin solution. Dilute 4 ml of *o*-phenanthroline ferrous sulphate solution as supplied by B.D.H. to 100 ml with distilled water in a graduated flask.

0.1% thoronol solution. Dissolve 250 mg of the sodium salt of 1-(*o*-arsenophenylazo)- 2-naphthol-3,6-disulphonic acid in 250 ml distilled water in a graduated flask.

Tartrate base solution. Dissolve 6 g of disodium tartrate and 0.15 g of sodium chloride in water and dilute to 50 ml.

Preparation of ion-exchange columns

Weigh out on a rough balance between 8 and 9 g of the air-dried Deacidite FF and transfer to a beaker. Place a cotton wool plug in the bottom of a 50 ml burette and half fill with water. Wet the resin thoroughly with water. Wash it into the burette and allow to settle with the water flowing slowly out of the burette tap. Do not allow the resin to dry out. Wash the column with 5*M* hydrochloric acid and allow to stand in this medium until ready for use.

Procedure

Weigh out 500 mg of sample and dissolve in 25 ml of (1 + 3) nitric acid in a suitable glass beaker. Evaporate the solution nearly to dryness. Cover the beaker with a watch glass and carefully add about 5 ml of concentrated hydrochloric acid. Boil vigorously until no more brown fumes are evolved, then remove the cover glass and evaporate to dryness. Add more concentrated hydrochloric acid and again evaporate to dryness. Dissolve the residue in 50 ml 5*N* hydrochloric acid and pass the solution through the ion-exchange column at a rate of 1 ml per minute, collecting the eluate in a 250 ml beaker. When all the solution has been transferred to the column, allow the liquid level to fall to the top of the resin column. Wash the sample beaker with 10 ml of 5*N* hydrochloric acid, transfer to the column and allow to pass through at 1 ml per minute. Repeat with four further 10 ml portions of 5*N* hydrochloric acid. Then add 5 ml of perchloric acid (60%) to the combined eluate and evaporate the solution to fumes of this acid. Add concentrated nitric acid dropwise to the fuming solution and continue with additions to effect the wet oxidation of organic matter in solution. Reserve this solution for the thorium determination. Recover the uranium from the column by the passage of five 10 ml portions of 0.2*M* hydrochloric acid, collecting the eluate in a 250 ml beaker. Evaporate this solution to fumes of a few millilitres of perchloric acid and remove organic matter by wet oxidation with nitric acid. Reserve this solution for the uranium determination.

Thorium determination

Thorium 5-10%. Dissolve the residue after wet oxidation in 2—3 ml of nitric acid (1 + 1) and accurately dilute the solution to 50 ml with water. Pipette a 20 ml aliquot into a 250 ml beaker and dilute to approximately 100 ml with water. Adjust the pH of the solution to the region of pH 3 to

3.5 and then add 4-5 drops of a 0.1% solution of pyrocatechol violet. Titrate the thorium directly with 0.02*M* EDTA added from a 10 ml calibrated burette graduated in 0.02 ml. Take the burette reading when the colour of the thorium pyrocatechol violet is just discharged*.

Thorium 1-5%. Dissolve the residue after wet oxidation in nitric acid and dilute to 50 ml with water as above. Pipette a 20 ml aliquot into a suitable beaker and dilute to 50 ml with water. Add 2 drops of the 0.1% pyrocatechol violet solution, after adjusting the pH of the solution to between 3 and 3.5. Titrate the thorium directly with 0.005*M* EDTA to the discharge of the thorium-pyrocatechol violet colour.

Thorium 0.1-1%. Dissolve the residue in 2-3 ml of hydrochloric acid (1 + 1) and dilute to 50 ml with water. Take a 5,10 or 25 ml aliquot, depending on the thorium content of the alloy, and evaporate to dryness in a small beaker. Dissolve the residue in 0.5 ml of concentrated hydrochloric acid and transfer the solution to a 50 ml flask with water. Then add 5 ml of the 0.1% thoronol solution and dilute to volume with water. Measure the absorbancy on the Spekker absorptiometer against a reference solution containing 0.5 ml of concentrated hydrochloric acid, 5 ml of 0.1% thoronol in 50 ml of solution. Take readings in 1 or 2 cm cells and use Ilford No. 605 filters in the instrument. Determine the thorium content by reference to a previously prepared calibration graph covering amounts of thorium up to 500 μg in the final 50 ml of solution. Prepare the calibration graph by applying the above procedure to suitable aliquots of a standard thorium nitrate solution. Evaporate each aliquot to dryness in a small beaker, then add 1 ml of perchloric acid (60%) and again evaporate to dryness. Dissolve the residue in 0.5 ml of concentrated hydrochloric acid and then form the thoronol colour as above.

Uranium determination

Uranium 1-10%. Treat the residue from the wet oxidation with 1 ml of concentrated hydrochloric acid and evaporate to dryness. Repeat this procedure twice to ensure the complete removal of nitric acid. For alloys in the lower range, dissolve the residue in 20 ml of 25% v/v hydrochloric acid and cool. For other alloys, prepare a hydrochloric acid solution of the uranium and take an aliquot containing from 5 to 10 mg of uranium. Adjust the volume and acidity to 20 ml and 25% v/v respectively. Pass the cooled uranium solution through the lead reductor, washing through with five 3 ml portions of 10% v/v hydrochloric acid. To the reduced solution, add 0.1 ml of 0.001*N* ferroin solution and 1 drop of phosphoric acid and then titrate with the standard ceric sulphate solution to the disappearance of the pink colour. Then add a further 9 drops of the phosphoric acid and 2-3 drops of the standard ceric solution to restore the full red colour of the indicator. Continue the titration carefully to the disappearance of the red colour. Correct the titre for a blank determined on the hydrochloric acid alone. Calculate the uranium content of the aliquot. 1 ml of 0.02*N* ceric sulphate is equivalent to 2.38 mg of uranium.

Uranium 0.1-1%. Make the volume of the solution after wet oxidation up to 50 ml with water. Then take an aliquot containing up to about 250 μg of uranium and evaporate just to dryness in a small beaker. Add 1 ml of water to the beaker followed by 0.5 ml of the tartrate base solution and warm the solution. Cool, add 1 ml of perchloric acid (60%) and dilute to 5 ml with water. Record the uranium polarogram occurring at —0.34 V *vs.* mercury pool anode with a square wave polarograph and obtain the uranium content by referring the uranium peak to a calibration graph or by the standard addition technique.

RESULTS AND CONCLUSIONS

The above procedure has been thoroughly tested by applying it to the determination of the uranium and thorium contents of synthetic alloy solutions containing accurately known amounts of these metals. Solutions of the alloys were prepared by dissolving the requisite amount of high purity bismuth metal in nitric acid. Then suitable aliquots of a uranyl nitrate solution and of a thorium nitrate solution were added to give the required composition. The uranium solution was prepared by dissolving Specpure U_3O_8 in nitric acid, whereas the thorium solution was prepared from AnalaR thorium nitrate, followed by standardisation employing the sebacate method[3]. In addition to the more usual alloy compositions, alloys were also taken at the extreme limits of composition so that the lowest percentages of uranium were determined in the presence of the maximum thorium contents and vice versa. All the results for the synthetic alloys by analysis are given in Table II. An examination of these results shows the good agreement in all cases between the amounts of thorium and uranium originally taken and the amounts finally recovered.

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* If the wet oxidation of organic matter is not complete, the colour change at the end-point may not be sharp. In such cases it is preferable to continue the addition of the EDTA solution to provide a slight excess and then to back titrate with a standard thorium nitrate solution until the indicator changes colour from yellow to purple. By this means the end-point may be approached from either direction several times if desired.

TABLE II

THE ANALYSIS OF SYNTHETIC BISMUTH – THORIUM – URANIUM ALLOYS

Total sample weight = 500 mg

Thorium				*Uranium*			
Wt. of metal mg		*Composition %*		*Wt. of metal mg*		*Composition %*	
taken	*recovered*	*synthetic*	*by analysis*	*taken*	*recovered*	*synthetic*	*by analysis*
46.80	46.71	9.36	9.34	5.0	5.0	1.0	1.0
23.40	23.34	4.68	4.67	25.0	24.99	5.0	4.99
4.68	4.69	0.936	0.94	50.0	49.75	10.0	9.95
46.80	46.60	9.36	9.32	2.50	2.40	0.50	0.48
46.80	46.50	9.36	9.30	0.50	0.46	0.10	0.09
2.34	2.35	0.47	0.47	50.0	49.9	10.0	9.98
0.468	0.475	0.094	0.095	50.0	49.7	10.0	9.94

TABLE III

RESULTS FOR ALLOYS SAMPLES

Sample No.	*Composition by analysis %*			
	Bismuth	*Thorium*	*Uranium*	*Total*
1	97.0	0.55	2.29	99.84
2	96.0	0.63	3.31	99.94
3	96.45	0.49	2.56	99.50
4	94.6	0.91	4.45	99.96
5	92.2	1.16	6.10	99.46

Table III contains results obtained in the analysis of some typical alloy samples. The alloys were dissolved in nitric acid and the bismuth content was obtained on a suitable aliquot by direct titration with EDTA using potassium iodide as indicator and sulphate to complex the thorium ions. To the sample aliquot, 5 ml of 2% potassium iodide and 5 ml of 10% sodium sulphate were added and then the volume was adjusted to about 100 ml with water. After the adjustment of the pH to the region of 1.5 to 2.0, titration of the bismuth with a standardised EDTA solution was carried out to the discharge of the bismuth-iodide colour. Satisfactory total compositions were obtained in all cases confirming the suitability of the procedure for alloy samples. The full procedure is not very rapid because of the need for the removal of organic matter taken into solution from the resin.

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SUMMARY

Procedures are described for the analysis of bismuth base alloys containing uranium and thorium in the range from 0.1 to 10%. The thorium is first separated by the passage of a solution of the sample in $5M$ hydrochloric acid through a column of Deacidite FF in the chloride form. For thorium contents greater than about 1%, the determination is completed volumetrically with EDTA using pyrocatechol violet as the indicator. Smaller amounts are determined absorptiometrically by the thoronol method. Uranium is recovered from the ion-exchange column in a quantity of $0.2M$ hydrochloric acid, bismuth still being retained by the column under these conditions. Uranium contents greater than about 1% are determined volumetrically after reduction to the tetravalent state with a lead reductor, whilst smaller amounts are determined polarographically using a tartrate base solution.

RÉSUMÉ

On décrit des procédés d'analyse d'alliages à base de bismuth contenant de l'uranium et du thorium dans les proportions de 0.1 à 10%.

Le thorium est séparé d'abord par le passage d'une solution chlorhydrique $5M$ de l'échantillon à travers une colonne de ,,Deacidite FF'' sous forme de chlorure. Pour des quantités de thorium dépassant 1%, la détermination est complétée volumétriquement par du EDTA, et en utilisant le pyrocatéchol violet comme indicateur. Les quantités plus faibles sont déterminées par absorption par la méthode au thoronol. L'uranium est récupéré de la colonne ,,échangeur d'ions'' dans l'acide chlorhydrique $0.2M$; le bismuth dans ces conditions est retenu par la dite colonne. Les quantités d'uranium, supérieures à 1% sont déterminées volumétriquement après réduction à l'état tétravalent avec un réducteur au plomb, tandis que les plus faibles quantités sont déterminées polarographiquement en utilisant une solution de tartrate.

ZUSAMMENFASSUNG

Es werden Verfahren zur Analyse von Wismuthlegierungen, die 0.1 bis 10 % Uran und Thorium enthalten, beschrieben. Das Thorium wird erst abgetrennt indem man eine Lösung der Probe in $5M$ Salzsäure durch eine Säule von Deacidit FF in der Chloridform leitet. Für Thoriumgehalte von mehr als ungefähr 1 % wird die Bestimmung volumetrisch mit EDTA unter Verwendung von Pyrokatechinviolett als Indikator beendet. Kleinere Mengen werden absorptiometrisch mittels der Thoronolmethode bestimmt. Das Uran wird aus der Ionenaustauschersäule mit $0.2M$ Salzsäure zurückgewonnen während das Wismuth unter diesen Bedingungen in der Säule zurückbleibt. Urangehalte die höher sind als 1% werden nach Reduktion in den vierwertigen Zustand mit Hilfe eines Bleireduktors, volumetrisch bestimmt, während kleinere Mengen polarographisch mit Hilfe einer Tartratlösung bestimmt werden.

REFERENCES

[1] G. W. C. Milner and J. W. Edwards, Atomic Energy Research Establishment, Report C/R 2143 (1956); *Anal. Chim. Acta*, 17 (1957) 259.

[2] K. A. Kraus and F. Nelson, *International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1955, Paper 837.

[3] T. O. Smith and C. James, *J. Am. Chem. Soc.*, 34 (1912) 281.

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THE CHROMATOGRAPHIC ANALYSIS OF ORGANIC PEROXIDES

by

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The problem often arises of detecting, identifying, and estimating in small amount the peroxidic products of the autoxidation or combustion of organic compounds. The usual chemical methods of detection, which depend on some oxidising reaction of the peroxides, are frequently unsuitable for quantitative application particularly for the dialkyl peroxides, and in the past identification of the peroxides has usually been possible only after their isolation[1,2,3]. We have found that organic peroxides can be identified in small amount by chromatography on treated paper, or by vapour-phase chromatography; the latter method in particular affords a convenient method of quantitative analysis.

PAPER CHROMATOGRAPHY

Experiments using untreated Whatman No. 1 or No. 4 paper were uniformly unsuccessful; by the ascending method all the solvents which were tried, except pentane, gave R_F values of unity for the peroxides listed in Table I. Pentane gave R_F values of zero, but mixed solvents containing pentane were unsuitable except for hydrogen peroxide. Attention was therefore directed to the treated papers having a less hydrophilic stationary phase.

Using paper treated with ethylene glycol and chloroform saturated with glycol as solvent[4], satisfactory R_F values were obtained for 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (0.74), 2-phenyl-2-butyl hydroperoxide (0.84), and hydrogen peroxide (0.58). The use of "reversed-phase" chromatography on silicone-treated paper by the following method, however, permits a wider choice of solvents.

Whatman No. 4 paper was soaked in a 5% solution of Silicone Fluid M.S. 1107 (Hopkin and Williams Ltd.) in cyclohexane, and then baked at 110° for 1 hour[5]. About 10 λ of a 1% solution of the peroxide was put on the base line, the paper equilibrated for 1 hour with the vapour of the lower layer of a mixture of water (6 vols.), ethanol (10 vols.) and chloroform (10 vols.), and then run with the upper layer by the ascending method* [5]. The spots were developed with a ferrous thiocyanate reagent which was prepared just before use by dissolving ferrous ammonium sulphate (0.7 g) in 10 cc of a solution of ammonium thiocyanate (5 g) and concentrated sulphuric acid (1 cc) in water (100 cc)[3]. This reagent will detect by a blood red colour less than 15 γ of a hydroperoxide, peroxyester, or diacyl peroxide, in a spot of 1 cm diameter. It is less sensitive for 9-xanthenyl peroxides and fails for triphenylmethyl peroxides and other dialkyl peroxides.

TABLE I

R_F VALUES OF ORGANIC PEROXIDES

	Peroxide	R_F
1	Hydrogen peroxide	0.84
2	Pinane hydroperoxide	0.61
3	1-Phenylethyl hydroperoxide	0.86
4	1-Phenylpropyl hydroperoxide	0.80
5	2-Phenyl-2-propyl hydroperoxide	0.85
6	2-Phenyl-2-butyl hydroperoxide	0.75
7	1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide	0.78
8	Decahydro-9-naphthyl hydroperoxide	0.50
9	Triphenylmethyl hydroperoxide	0.19
10	Tri(*p*-nitrophenyl)methyl hydroperoxide	0.14
11	*tert.*-Butyl perbenzoate	0.17
12	*tert.*-Butyl diperterephthalate	0.16[a]
13	Benzoyl peroxide	0.00[b]
14	Diphenylmethyl 9-xanthenyl peroxide	0.16

[a] The spot has a tail reaching back to the base line, probably indicating hydrolysis to the monoperester.

[b] After spraying, the spot develops slowly over 1 hour.

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* This method of preparation of the solvent is wasteful of the large lower layer. A more economical solvent is a mixture of chloroform (2 vols.), water (20 vols.), and ethanol (17 vols.), which is homogeneous; the paper is equilibrated with the vapour of wet chloroform. This method gives slightly lower R_F values than those quoted in Table I.

Table I records the R_F values of a number of peroxides. On the same batch of paper, these values could be reproduced with an accuracy of about 0.02 units; 2-phenyl-2-propyl hydroperoxide, which is commercially available, would be a suitable internal standard for deriving relative R_F values.

By this method the hydroperoxides which are present in small amount in hydrocarbons have been identified.

Peroxides of low molecular weight such as *tert.*-butyl and *tert.*-pentyl hydroperoxides are too volatile to be treated by the above method, and are lost from the paper during running and during drying. MINKOFF *et al.*[6] solved this difficulty by enclosing the paper between glass plates during running, and by spraying the wet chromatogram immediately it was removed. Our attempts with silicone-treated paper by this method have not been successful but we have found that these volatile peroxides can readily be identified and estimated by vapour-phase (gas-liquid) partition chromatography.

VAPOUR-PHASE CHROMATOGRAPHY

A commercial instrument made by Messrs. Griffin and George Ltd., London, was used. The column, 185 × 0.7 cm, was packed with 20-mesh purified kieselguhr (Johnson Manville "Celite 545") coated with 30% of dinonyl phthalate. Nitrogen or air was used as the carrier gas; liquid samples of about 0.1 cc were introduced onto the column with a micrometer syringe through a rubber vaccine cap, and detected in the eluate with a katharometer connected to an automatic recording potentiometer.

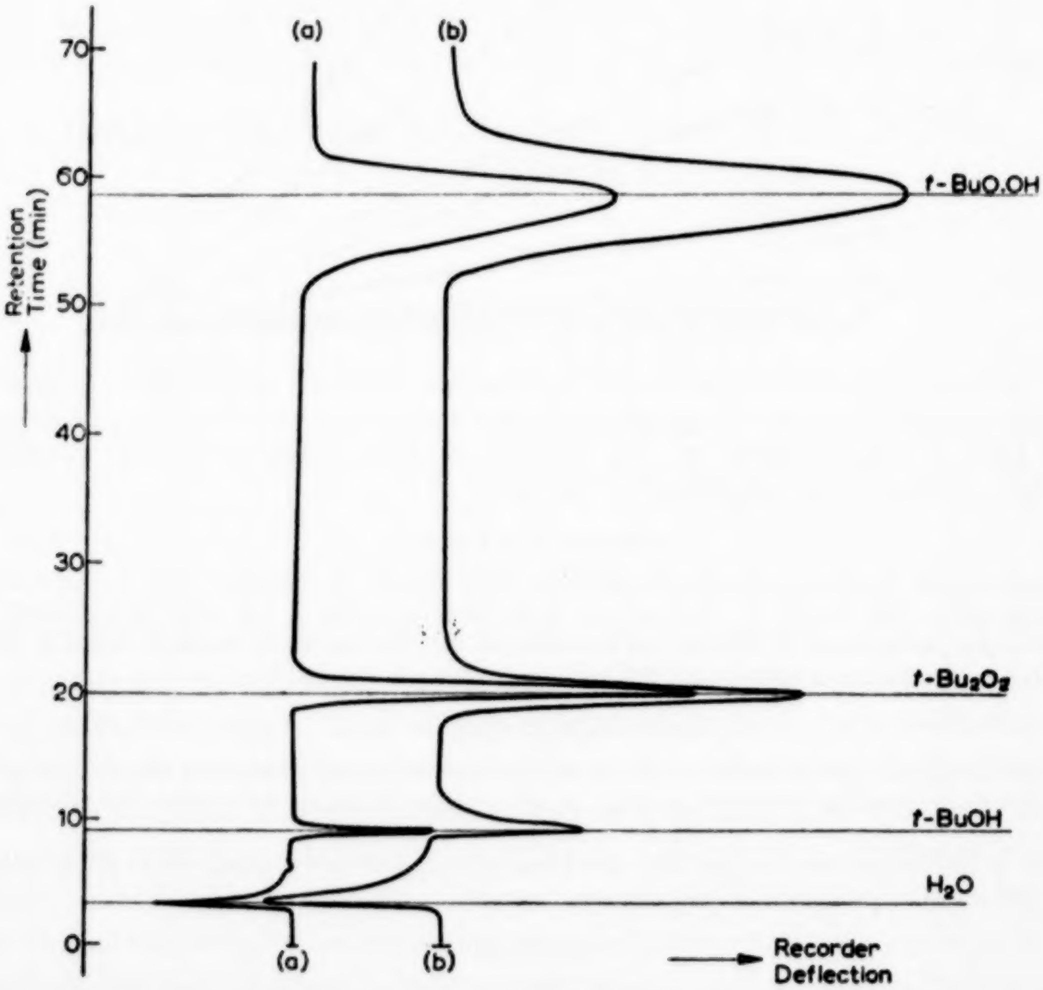

Fig. 1. Gas-liquid partition chromatography. Separation of (a) commercial 60% *tert.*-butyl hydroperoxide, and (b) a synthetic mixture of *tert.*-butyl hydroperoxide (0.5653 g), di-*tert.*-butyl peroxide (0.2333 g), *tert.*-butyl alcohol (0.0169 g), and water (0.0067 g).
Column temperature, 78°. Carrier gas, air, 1.35 l/h.

Fig. 1 shows the trace (a) obtained with commercial 60% *tert.*-butyl hydroperoxide, which can be analysed quantitatively by comparing the areas under the peaks with those of the calibration curve (b) of the synthetic mixture of the components.

Fig. 2 records the relative retention times referred to di-*tert.*-butyl peroxide as an internal standard, of the peroxides and other products obtained by the autoxidation of some *tert.*-alkyl metallic compounds. Benzene, methyl ethyl ketone, and *p*-xylene have been included as further internal standards[7]. If a transparent copy of this graph is superimposed on the potentiometer trace of reaction products the components can readily be identified, whatever the flow rate, by the coincidence of the position of the peaks on the base line, with the diagonal lines.

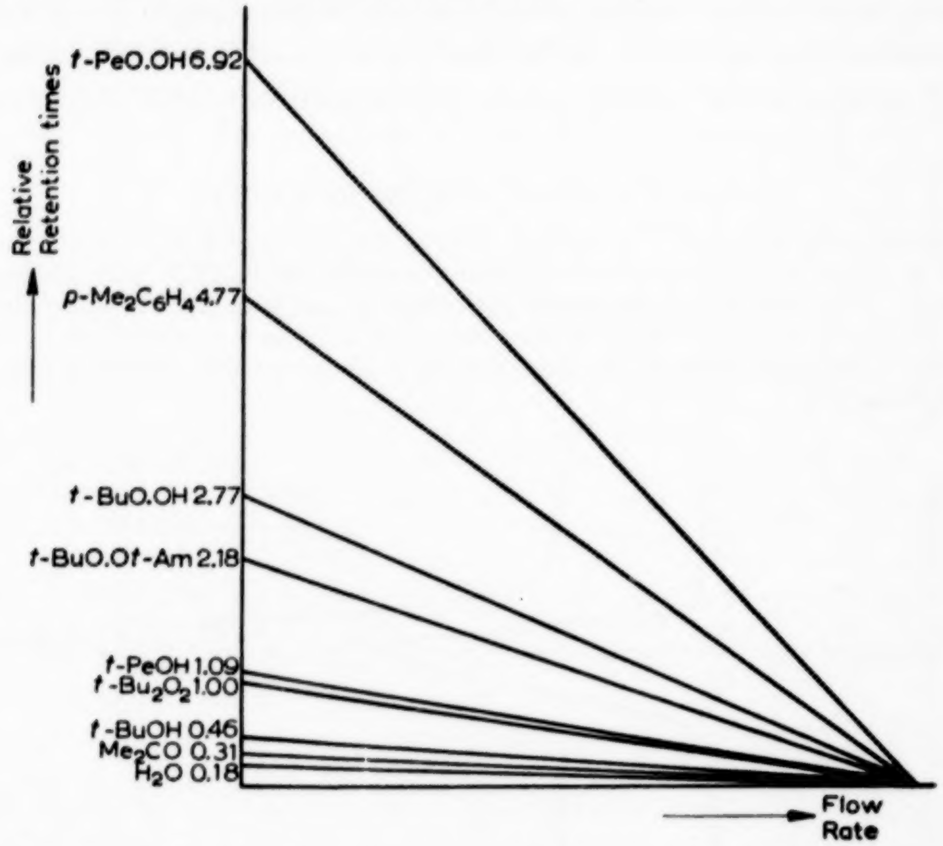

Fig. 2. Relative retention times of organic peroxides. Carrier gas, air. The use of nitrogen as the carrier gas gave the same values for the relative retention times. Values for further internal standards are: benzene, 0.91; methyl ethyl ketone, 0.66.

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SUMMARY

Organic peroxides can be identified by reversed-phase chromatography on silicone-treated paper; a chloroform-ethanol-water mixture is used as solvent, and the spray reagent is acidified ferrous thiocyanate.

Peroxides of low molecular weight are lost from the paper by volatilisation; these can be identified and estimated by vapour-phase chromatography.

RÉSUMÉ

Les peroxydes organiques peuvent être identifiés par chromatographie sur papier traité au silicone; un mélange chloroforme-éthanol-eau est utilisé comme solvant et le réactif révélateur est le thiocyanate ferreux acidifié.

Les peroxydes de poids moléculaire faible s'échappent du papier par évaporation; ils peuvent être identifiés et dosés par chromatographie en "phase-vapeur".

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ZUSAMMENFASSUNG

Organische Peroxyde können durch Chromatographie an mit Silicon vorbehandeltem Papier identifiziert werden; als Lösungsmittel dient ein Gemisch Chloroform-Äthanol-Wasser und als Entwickler angesäuertes Eisen(II)thiocyanat.

Peroxyde mit niedrigem Molekulargewicht gehen durch Verdampfen aus dem Papier verloren; diese können durch Dampfphasenchromatographie identifiziert und bestimmt werden.

REFERENCES

[1] R. Criegee, in Houben-Weyl, *Methoden der Organischen Chemie*, Vol. 2, Georg Thieme & Cie, Stuttgart, 1953, p. 568.

[2] A. G. Davies, *J. Roy. Inst. Chem.*, 80 (1956) 386.

[3] A. C. Egerton, A. J. Everett, G. J. Minkoff, S. Rudrakanchana and K. C. Salooja, *Anal. Chim. Acta*, 10 (1954) 422.

[4] A. Zaffaroni, R. B. Burton and E. H. Keutmann, *Science*, 111 (1950) 6.

[5] T. H. Kritchevsky and A. Tiselius, *ibid.*, 114 (1951) 299.

[6] G. J. Minkoff, H. Bruschweiler and K. C. Salooja, *Nature*, 172 (1953) 909.

[7] *Vapour Phase Chromatography*, Ed. by D. H. Desty, Butterworths Scientific Publications, London, 1957, p. xi.

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THE MICRO-HETEROMETRIC DETERMINATION OF SILVER WITH *p*-DIMETHYLAMINO-BENZYLIDENE-RHODANINE

DIRECT DETERMINATION OF TRACES OF SILVER IN ALLOYS AND SOLUTIONS

by

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INTRODUCTION

The use of dimethylamino-benzylidene-rhodanine (= DBR) as a spot test reagent for silver was made first by Feigl, during a study of the behaviour of rhodanine towards silver, gold, palladium, etc.[1]. The silver salt is very insoluble. Later colorimetric methods were elaborated for the determination of silver[2]. This determination is always carried out in acid solution. The accepted view is that the specificity of the reagent is lost in neutral or basic solutions. Our aim was to study the reaction heterometrically. The DBR is only very sparingly soluble in organic reagents such as acetone or ethyl alcohol. In acid solution the reagent is precipitated on addition of water; on the other hand, a clear yellow solution of the reagent was obtained by us in ammoniacal solution. In order to avoid interference of the reagent, all our experiments were therefore carried out in ammoniacal solution. We also found that in the ammoniacal solution no interference whatever was caused by the presence of large amounts of chloride. From this report it may be taken that, given the observation of working conditions and the use of a suitable complexing agent, 0.05 to 0.1 mg silver in 20 ml solution can be determined heterometrically in 5 minutes with an error of 0–1.5%. No previous separation whatever is necessary, and the analysed solution may contain 99 to 99.9% of any foreign metal. Rare earths such as thorium, cerium, zirconium or uranium make no exception.

It seems to us that the method presented is of *universal application for the quick and safe heterometric determination of silver (2-3 γ/ml) in other metals or solutions.* Our investigation was partly devoted to the determination of silver in palladium, gold or platinum. In all cases one compound only was obtained, the composition being $Ag_1(DBR)_1$.

EXPERIMENTAL

A 0.002*M* DBR stock solution in acetone was prepared. This solution was then diluted in an approximately sixfold amount of ethyl alcohol. More dilute solutions were prepared by diluting this solution in alcohol. An alcoholic solution was used because of the higher boiling point. The solutions obtained were stable for a long period. The DBR was a Hopkin and Williams reagent for spot tests. All other chemicals were either AnalaR or chemically pure reagents.

The same working conditions were observed as in previous heterometric investigations[3,4]. The titrations were carried out at 20°C. The reaction vessel, which was thermostatically controlled, had a diameter of about 4 cm. The stirring, which was vigorous, was electronically controlled and was more or less uniform in all experiments. All measurements were made using a Fisher (Corning) (bluish-) green filter (525). The same filter is regularly supplied with the Fisher Electrophotometer and has a maximum transmission at about 525 mμ. We found that the use of this filter was essential. Under the same conditions, the use of yellowish-green Corning filters was not satisfactory and gave a low maximum-density value.

RESULTS

Light

Experimenting with DBR blank solutions, we came to the conclusion that only in ammoniacal solutions were clear solutions of DBR always obtained. We naturally have to consider the yellow colour of the reagent itself, the light absorption of which depends on the filter chosen. On the other hand, the silver-DBR precipitate is also of an intense red colour, and its absorption, therefore, also depends on the filter used. Hence, it would be difficult to measure the absorption of the precipitate alone, and we indeed measured a mixed effect of the suspension with light of different colours. Table I and Fig. 1 (expts. 1-6), show some of the results obtained. At first, titrations were carried out using a somewhat more concentrated solution of silver nitrate (expts. 1-4). Good results were obtained even without using a filter at all (expts. 1 and 2). The error was close to zero, and after the first maximum-density point a horizontal density line was obtained. Working with a red filter under the same conditions, the maximum-density value was very low and no clear end-point at all was obtainable (expt. 3). A similar effect was obtained using a yellowish-green Corning filter. We then used a Fisher (-Corning) green filter (525), and the maximum-density value obtained was very high (expt. 4). A blank titration carried out in the absence of silver with the same Fisher green filter (expt. 5), showed that even a considerable excess of unreacted DBR gave a relatively low density, so that the main absorption was caused by the precipitation of silver. The following heterometric titrations (expts. 7-13) were therefore carried out with the Fisher green filter, but with more diluted solutions of silver nitrate and DBR. The additional effect of the excesses of DBR was thus still further reduced. Indeed,

TABLE I

Composition: *a* ml $AgNO_3$ + *b* ml supplements + (20 — *a* — *b*) ml H_2O + *x* ml DBR (alc.). Concentration of Ag: $1.5 \cdot 10^{-4}M - 5 \cdot 10^{-5}M$. Content Ag: 0.108 mg–0.065 mg. Titration time = 4–5 min, temp. = 20°C.

Expt. number	*$AgNO_3$*		*Supplements*	*Found*				
	ml	*molarity*		*DBR ml (= x)*	*DBR molarity*	*Max. density value*	*Error %*	*Remarks*
1	3	0.001	0.5 ml conc. NH_4OH + 2 ml $M NH_4NO_3$	3.00 h	0.001	0.36	0.0	no filter
2	3	0.001	0.5 ,, ,, ,, +1 ,, 0.1M ,,	i 3.00 h	0.001	0.40	0.0	,, ,,
3	3	0.001	0.5 ,, ,, ,, +2 ,, M ,,			0.13		red filter
4	3	0.001	0.5 ,, ,, ,, +2 ,, ,, ,,			1.5		green filter Fisher
5	—	—	0.5 ,, ,, ,, +2 ,, ,, ,,	2	0.001	0.33		,, ,, ,,
6	3	0.00033	0.5 ,, ,, ,, +2 ,, ,, ,,	c 3.05 h	0.00033	0.70	1.6	,, ,, ,,
7	3	,,	0.5 ,, ,, ,, +1 ,, 0.1M ,, +5 ml M Na_2-tartrate	i 3.05 h	,,	0.72	1.6	,, ,, ,,
8	3	,,	0.5 ,, ,, ,, +1 ,, ,, ,, +5 ml M Na_3-citrate	i 2.95 h	,,	0.76	1.6	,, ,, ,,
9	3	,,	0.5 ,, ,, ,, +1 ,, ,, ,, +5 ml 0.2M Na_2-EDTA	i 3.00 h	,,	0.77	0.0	,, ,, ,,
10	3	0.0002	0.5 ,, ,, ,, +1 ,, ,, ,, +5 ml M Na_3-citrate	i 3.03	0.0002	0.51	1.0	,, ,, ,,
11	3	,,	0.5 ,, ,, ,, +1 ,, ,, ,, +8 ml M NaCl	i 3.00 h	,,	0.48	0.0	,, ,, ,,
12	3	,,	0.5 ,, ,, ,, +1 ,, ,, ,,	i 3.03	,,	0.51	1.0	,, ,, ,,
13	3	0.00033	0.5 ,, +1 ,, ,, ,, +1 ml 0.1M KCN			0.23		,, ,, ,, , yellow sol.

i = intersection point; c = contact point; h = horizontal maximum-density line.

in almost all titrations, a horizontal maximum-optical-density line was obtained after the end-point of the titration.

Complexing agents

A study was made of the influence of different complexing agents, later used for the determination of silver in the presence of foreign metals. In strong ammoniacal solutions neither tartrate, citrate nor Na_2-EDTA had a noticeable influence on the results of the titrations (expts. 7-9). The amount of analysed silver was still further reduced and normal maximum-density values were even obtained analysing 0.06 mg silver in 20 ml solutions (expts. 10-12). In the presence of potassium cyanide (expt. 13), only a yellow solution was obtained. No harm whatever was caused by the presence of considerable amounts of chloride (expt. 11) and the maximum-density value remained unchanged.

The presence of foreign metals

Table II and Fig. 2 give the composition and results of a small number of experiments carried out in the presence of large excesses of foreign cations. We have omitted many experiments which proved unsatisfactory, although their results were sometimes very instructive, and pointed the way for further investigation. Generally, the silver made up 0.05-0.1% of the total metal content. The error in the determination of silver was

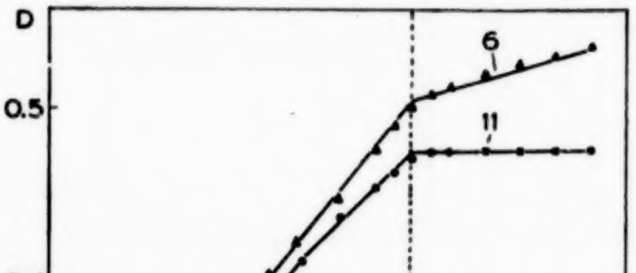

Fig. 1. Titrations of silver nitrate with dimethyl-amino-benzylidene-rhodanine.

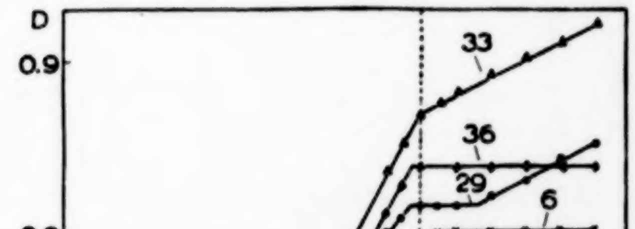

Fig. 2. Titrations of silver nitrate with dimethyl-amino-benzylidene-rhodanine.

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TABLE II

Composition: 3 ml 0.00033M $AgNO_3$ + a ml supplements + (17—a) or (27—a) ml H_2O + x ml 0.00033M DBR (alc.). Content Ag: 0.108 mg. Titration time 5 min, temp.: 20°C. Filter: Fisher green filter (525).

Expt. number	Supplements	Volume ml	Ag %	Found		
				ml(= x) DBR	Max. density value	% Error
14	0.5 ml conc. NH_4OH + 2 ml M NH_4Cl + 5 ml M Na_3-citrate + 2 ml M $CaCl_2$	20	0.12	i 2.97 h	0.76	1.0
15	0.5 ,, ,, ,, + 2 ,, ,, NH_4NO_3 + 5 ,, ,, ,, + 2 ,, ,, $Co(NO_3)_2$	,,	0.12	,, 2.95 ,,	0.66	1.6
16	,, ,, ,, + 2 ,, ,, NH_4Cl + 5 ,, ,, ,, + 1 ,, ,, $BaCl_2$	,,	0.07	,, 2.97 ,,	0.70	1.0
17	0.5 ,, ,, ,, + 2 ,, ,, NH_4NO_3 + 5 ,, ,, ,, + 2 ,, ,, $Mg(NO_3)_2$	,,	0.2	,, 3.00 ,,	0.69	0.0
18	0.5 ,, ,, ,, + 1 ,, 0.1M ,, + 5 ,, ,, ,, + 2 ,, ,, $Zn(NO_3)_2$	,,	0.07	,, 2.97 ,,	0.74	1.0
19	0.5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, $MnSO_4$	,,	0.2	,, 3.00 ,,	0.77	0.0
20	0.5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, +0.5,, ,, $Ni(NO_3)_2$	,,	0.34	,, 2.93 ,,	0.78	2.0
21	0.5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, +0.5,, ,, $Co(NO_3)_2$	,,	0.33	,, 3.03 ,,	0.63	1.0
22	0.5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, Na_2-tartrate + 1 ,, ,, $Al(NO_3)_3$	,,	0.37	,, 2.97 ,,	0.72	1.0
23	0.5 ,, ,, ,, + 1 ,, M ,, + 5 ,, ,, ,, + 2 ,, ,, ,,	30	0.18	,, 2.90 ,,	0.86	3.3
24	0.5 ,, ,, ,, + 1 ,, 0.1M ,, + 5 ,, ,, ,, + 2 ,, 0.1M $Cr(NO_3)_3$	20	1.0	,, 3.00 ,,	0.80	0.0
25	0.5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, + 5 ,, ,, ,, $Fe(NO_3)_3$	,,	0.35	,, 2.99 ,,	0.72	0.3
26	0.5 ,, ,, ,, + 1 ,, M ,, + 5 ,, ,, ,, + 1 ,, M ,,	30	0.18	,, 2.94 ,,	0.72	2.0
27	0.5 ,, ,, ,, + 1 ,, 0.1M ,, + 5 ,, ,, Na_3-citrate + 1 ,, ,, $Pb(NO_3)_2$	20	0.05	,, 3.03 ,,	0.68	1.0
28	0.5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, + 1 ,, ,, $Cu(NO_3)_2$	,,	0.16	,, 3.00 ,,	0.84	0.0
29	0.5 ,, ,, ,, + 1 ,, M ,, + 5 ,, ,, ,, + 2 ,, ,, ,,	,,	0.08	,, 2.95 ,,	>0.82	1.6
30	1.0 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, + 2 ,, 0.4M $SbCl_3/HCl$	,,	0.1	,, 2.95 ,,	0.76	1.6
31	1.0 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, ,, ,, +0.5,, M $Bi(NO_3)_3/HNO_3$	,,	0.1	,, 3.03 ,,	0.74	1.0
32	0.5 ,, ,, ,, + 1 ,, 0.1M ,, + 5 ,, ,, Na-tartrate + 5 ,, 0.2M $UO_2(NO_3)_2$	30	0.04	,, 2.98 ,,	0.78	0.6
33	0.5 ,, ,, ,, + 1 ,, M ,, + 7 ,, 0.2M Na_2-EDTA + 4 ,, 0.2M $Hg(NO_3)_2$	,,	0.06	,, 3.00 ,,	>0.87	0.0
34	0.5 ,, ,, ,, + 1 ,, 0.1M ,, + 5 ,, M Na_2-tartrate + 5 ,, 0.1M $ZrO(NO_3)_2$	,,	0.22	,, 2.95 ,,	0.81	1.6
35	0.5 ,, ,, ,, + 1 ,, M ,, + 5 ,, ,, ,, + 5 ,, 0.1M $Ce(NO_3)_3$	30	0.14	,, 3.04 ,,	0.81	1.3
36	0.5 ,, ,, ,, + 1 ,, 0.1M ,, + 5 ,, ,, ,, + 5 ,, 0.1M $Th(NO_3)_4$	,,	0.09	,, 2.95 ,,	0.84	1.6
36a	0.5 ,, ,, ,, + 1 ,, M ,, +10 ,, 0.2M Na_2-EDTA + 5 ,, 0.1M $TlNO_3$	20	0.09	,, 2.97 ,,	0.82	1.0

i = intersection point; h = horizontal maximum-density line.

never higher than 2% but in most cases the error was between zero and 1%. In all cases without exception the sensitivity of the titration was independent of the foreign metal present. The molar amounts given in the table were in the main almost the highest amount of metal which could be present without interfering with a safe fixation of the end-point. The latter was, in all these experiments, determined by the *intersection* of the last part of the titration density line with the maximum line obtained *after* the end-point (= i). The maximum-density line was almost always horizontal (= h). Only if the amount of foreign metal present was above the permissible limit of concentration did the maximum-density line cease to be horizontal and the densities obtained (= 0.05 mg silver in 20 ml solution) tended either to rise or fall.

Percentage of foreign metal

Table II provides the following results. The maximum-density values obtained were between 0.7 and 0.8. It was, therefore, still quite possible to analyse about half the amount of silver used. This, however, must evidently be the limit. Hence it was also possible to reduce the concentration of the titrant to $0.0002M$. In those cases in which the maximum-density line tended to increase (expts. 29 and 33) or decrease, the effect would be reduced using a more dilute solution of titrant. By reducing the amount of silver to half, the percentage of silver present would automatically be reduced in all cases to half the value given in the table.

In cases in which a precipitate appeared before the beginning of the titration, we found it helpful to work with a reacting solution of 30 instead of 20 ml. The composition and amount of silver was the same. This was also very useful in many other cases in which the maximum-density line was no longer horizontal.

As to the results of titration which were obtained using higher concentrations of foreign metals than those cited in Table II, the following may be said. In the case of *manganese* a maximum-density point was obtained at the end of the titration, and on further addition of titrant, the density values decreased rapidly. In the presence of double amounts of *nickel* the end-point became less dependable and the densities tended to decrease. If the amount of *cobalt* was doubled, the end-point was obtained too early and the error was higher than usual. In the presence of larger amounts of *aluminium* (expt. 23), even if titrated in 30 ml volume, the end-point was obtained somewhat too early. In the case of *chromium* (expt. 24), a precipitate appeared before the titration. Only when working with 30 ml volume was a reliable end-point obtained in the presence of *iron* (expt. 26), otherwise only a maximum-density point was obtained, after which the density values decreased considerably. In the presence of *copper* (expt. 29), the maximum-density line was short and then the densities increased continuously. The addition of more citrate did not improve the result. *Mercuric mercury*, even if present in very dilute solution, gave, in the presence of citrate, tartrate or chloride, a continuously rising density titration line. Contrary to this, even in the presence of large amounts of mercury, we obtained a normal titration curve in the presence of Na_2-EDTA (expt. 33). Just the same was observed in the presence of thallium (I). Satisfactory results were obtained only in Na_2-EDTA solution (expt. 36a).

The influence of large excesses of foreign metals depends only upon *the molar amount of the foreign metal*. With this in mind, we may conclude that the percentage of silver is exceedingly small in the presence of the following metals: thorium, uranium, mercury,

TABLE III

Composition: 3 ml 0.00033M $AgNO_3$ + a ml supplements + (17—a) ml H_2O + x ml 0.00033M DBR (alc.). Content Ag: 0.108 mg. Titration time: 5 min, temp.: 20°C. Filter: Fisher green filter (525).

Expt. number	*Supplements*	*Found*			
		% Ag	*ml (= x) DBR*	*Max. density value*	*% Error*
37	2 ml 0.004M $PdCl_2$ + 1 ml M NH_4NO_3 + 0.5 ml conc. NH_4OH	7.7	i 3.03 h	0.75	1.0
38	5 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,,	4.9	,, 3.00 ,,	0.72	0.0
39	5 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 1 ml 0.1M dimethylglyoxime	4.9	,, 3.00 ,,	0.75	0.0
40	5 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, M Na_3-citrate	4.9	,, 2.9 ,,	0.73	3.0
41	2 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 4 ,, 2M NaCl	11.2	,, 2.97 ,,	0.72	1.0
42	2 ,, 0.001 ,, $AuCl_3$ + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, M Na_3-citrate	21.5	,, 2.94 ,,	0.73	2.0
43	5 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, ,, ,,	10.2	,, 2.9	0.71	3.0
44	1 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 1 ,, 0.01M dimethylglyoxime			0.71	
45	2 ,, ,, ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 4 ,, 2M NaCl		,, 2.9	0.72	
46	1 ,, 0.002 ,, H_2PtCl_6 + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 4 ,, 2M ,,		2.8	0.77	
47	1 ,, 0.004 ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, M Na_3-citrate	10.8	,, 3.00 h	0.77	0.0
48	4 ,, 0.004 ,, ,, + 1 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, ,, ,,	2.7	,, 2.98 ,,	0.80	0.6

i = intersection point; h = horizontal maximum-density line.

lead and bismuth. In all these cases about 0.02 to 0.04% silver in the metal may be determined directly with an error of less than 2%. In zinc or copper, also, the percentage of silver may be ∿ 0.04%.

In almost all other cases cited in Table II, the percentage of silver was 0.1%-0.2%.

Supplements

Two kinds of supplements were used, one being essential for the determination solely of silver, the other being composed mostly of specific complexing agents. The following must be pointed out regarding these specific complexing agents: 0.5 ml conc. NH_4OH was amply sufficient in most cases, but in the presence of antimonium or bismuth which are held in solution only in a more concentrated acid solution, more ammonia was used. Regarding the amount of NH_4NO_3 which has to be present, we found that in many cases the titration was better and the horizontal maximum-density line more constant when 1 ml M NH_4NO_3 was used instead of 1 ml 0.1M NH_4NO_3. The amount of NH_4NO_3 cited in the table was, therefore, not decisive. If many foreign metals requiring different complexing agents are present simultaneously in the analysed solution, a mixture of the complexing agents must be used. It is therefore very important to notice in Table I that all the complexing agents concerned were used successfully in the ammoniacal silver solution. From previous investigations we already knew that basic citrate or tartrate forms very stable complexes with most metals. In the case of bivalent metals, citrate was used. We found that in the presence of polyvalent metals the citrato-complexes formed are, in many cases, less soluble than the corresponding tartrato-complexes, while the stability of the complex is probably equal in both cases. All foreign metals with the exception of thallium and mercuric mercury were in this way effectively masked. Potassium cyanide could not be used since the silver was dissolved under our working conditions. The presence of large amounts of sodium chloride was also ineffective. We found that mercuric mercury and thallium could be complexed in the ammoniacal solution of Na_2-EDTA (expts. 33 and 36a).

The presence of palladium, gold or platinum

Special attention was drawn to the determination of silver in precious metals. All the complexing agents used in Table I were tested. It must be borne in mind that ammonia itself forms very stable complexes with the metals concerned. A small selection of results is presented in Table III. The presence of *palladium* (∿ 95%) (Table III, expts. 37-41) caused scarcely any difficulty in the determination of silver. All the complexing agents gave almost equally good results. Even ammonia used alone may be sufficient.

Greater difficulties were encountered in the presence of *gold* (Table III, expts. 42-45), the results being successful only in the presence of citrate (expts. 42 and 43). The solutions contained 10%-20% silver. After the end-point had been reached the density line rose, the increase being parallel to the amount of the gold present. Reversely, in solutions containing somewhat less gold the deteriorating effect disappeared.

A few results obtained in the presence of *platinum* are also presented (Table III, expts. 46-48). Citrate appears to be the best complexing agent. Even if the platinum composed more than 95% of the total (expt. 48), the determination was very successful and errors were confined to between 0 and 1 %.

METHOD

General remarks

All titrations throughout the series of experiments were conducted using a Fisher green filter (525). The end-point of the titration was always obtained by the intersection of the line drawn through the points of the last part of the titration curve with the maximum-density line.

Titration time: 5 minutes. Error: 0-1.5%.

1. In the absence of foreign metals

20 ml aqueous solution, containing 0.05 to 0.1 mg silver, in addition to 1 ml 0.1-1.0*M* NH_4NO_3 and 0.5 ml conc. NH_4OH, is titrated heterometrically with a solution of 0.0002-0.0003*M* dimethylamino-benzylidene-rhodanine (alc.) (= DBR).

2. In the presence of mono- or bi-valent metals

20 ml aqueous solution, containing 5 ml *M* Na_3-citrate (or $\sim$ 2 g Na_3-citrate·$5H_2O$), 1 ml 0.1-1.0*M* NH_4NO_3, 0.5 ml conc. NH_4OH, and up to 99.9% of any foreign metal, is titrated heterometrically with a solution of 0.0002-0.0003*M* DBR (alc.).

Remark. In the presence of thallium or mercuric mercury the citrate must be replaced by 5 to 10 ml of 0.2*M* Na_2-ethylenediamine-tetraacetate.

3. In the presence of polyvalent metals

In the presence of aluminium, chromium(III), iron(III), uranium(VI), zirconium, thorium or cerium(III), the citrate should be replaced by Na_2-tartrate. In the presence of antimonium(III) or bismuth (III) proceed as in (2), adding 1 ml conc. NH_4OH. In the presence of gold(III), platinum (IV) or palladium(II) proceed as in (2).

SUMMARY

A heterometric method was presented for the direct determination of 0.05-0.1 mg silver in 20 to 30 ml solution. The solution contained, besides complexing agents, 99.7 to 99.9% of the following metals: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr (99%), Fe(III), Pb, Cu, Sb, Bi, U, Hg, Zr, Ce, Th, Tl. The error was 0.0-2.0%. It was possible to determine the same amount of silver in solutions of Pd ($\sim$ 95%), Au(III) ($\sim$ 90%) or Pt(IV) ($\sim$ 97%) with an error of 0.0-3.0%.

A full titration always lasted *ca.* five minutes.

RÉSUMÉ

Une méthode hétérométrique est présentée pour la détermination de 0.05-0.1 mg d'argent dans 20 à 30 ml solution. La solution contenait, à part les agents complexants, 99.7 à 99.9% des métaux suivants: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr (99%), Fe(III), Pb, Cu, Sb, Bi, U, Hg, Zr, Ce, Th, Tl. L'erreur est de 0.0-2.0%. La même quantité d'argent peut être aussi déterminée dans des solutions contenant Pd ($\sim$ 95%), Au(III) ($\sim$ 90%) ou Pt(IV) ($\sim$ 97%). L'erreur est de 0.0-3.0%.

Un titrage entier dure environ cinq minutes.

ZUSAMMENFASSUNG

Eine heterometrische Methode wurde präsentiert für die direkte Bestimmung von 0.05-0.1 mg Silber in 20 bis 30 ml Lösung. Die Lösung enthielt, von komplexbildenden Körpern abgesehen, 99.7 bis 99.9% folgende Metalle: Ca, Ba, Mg, Zn, Mn, Ni, Co, Al, Cr (99%), Fe(III), Pb, Cu, Sb, Bi, U, Hg, Zr, Ce, Th, Tl. Fehler 0.0-2.0%. Dieselbe Menge Silber kann in Lösungen von Pd ($\sim$ 95%), Au(III) ($\sim$ 90%) oder Pt(IV) ($\sim$ 97%) bestimmt werden. Fehler 0.0-3.0%.

Eine volle Titration dauert 5 Minuten.

REFERENCES

[1] F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press Inc., 1949, p. 328.

[2] E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., 1950, p. 540.

[3] See literature on heterometry 1953-1956 in *Anal. Chim. Acta*, 16 (1957) 75.
M. Bobtelsky and R. Rafailoff, *ibid.*, 17 (1957) 308.
M. Bobtelsky and J. Eisenstadter, *ibid.*, 16 (1957) 479.

[4] M. Bobtelsky, *ibid.*, 13 (1955) 172.

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POTENTIOMETRIC TITRATIONS IN NON-AQUEOUS SOLUTION

III. DIRECTIONS FOR CHOOSING SOLVENT-TITRANT COMBINATIONS

by

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This paper is intended to facilitate the practical application of the material collected in two previous papers, which deal in a more fundamental way with the acidity potential scale of twelve solvents[1], and the anomalous behaviour of weak oxygen acids[2].

An extremely simplified consideration of the basic ideas is presented here, together with a series of tables containing recommended solvent-titrant combinations for titrations of various types of acids and bases.

APPARATUS

The indications given in this paper are based on the use of Beckman glass and calomel electrodes and a Beckman model G pH meter. Preferred types of electrodes are 1190-75 or 1190-80 glass electrodes and a 1170 calomel electrode. As different types of glass may show considerable differences in response to non-aqueous solutions, other types of glass electrodes, should be thoroughly tested before being used. The glass electrodes should be kept in water when not in use.

Titration vessels and burettes can be adapted to the requirements of a particular application. Magnetic stirring is preferred. The stirring device should be electrically shielded, since otherwise partial or complete insensitivity of the measuring system may develop.

SUPPORTING ELECTROLYTES

In media of low conductivity, especially in the inert and weakly basic solvents, potentiometer stability may be improved by the addition of a supporting electrolyte.

Tetraalkylammonium iodides* in a concentration of 1 millimole per liter will serve this purpose for all titrations in pyridine, and for titrations in inert solvents of acids having a $pK_{\mathrm{water}} > 2$.

With strong acids ($pK_{\mathrm{water}} < 2$), the iodides react in inert solvents to yield hydrogen iodide. This is oxidized (*e.g.* by the strong acid itself) to iodine, which, in turn, is hydrolyzed by the strongly basic titrant. As a consequence, extra inflections appear in the titration curve. For such titrations the corresponding perchlorates or *p*-toluene sulphonates might be suitable as supporting electrolytes. Alkali metal salts cannot be used, since they may interfere with the proper functioning of the glass electrode[3].

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* With the exception of tetramethylammonium iodide, which dissolves with difficulty in pyridine.

SOLVENTS

Every solvent has a characteristic acidity potential range, which is related to its own acidity and basicity. The acidity potential ranges of eight solvents particularly recommended for use are given in Fig. 1. They apply to titrations, in which the Beckman glass and calomel electrodes are used, of acids and bases in a concentration of approximately 0.01N. Table I presents these eight solvents (in italics) and some less generally applicable alternatives, together with indications and references regarding their purification.

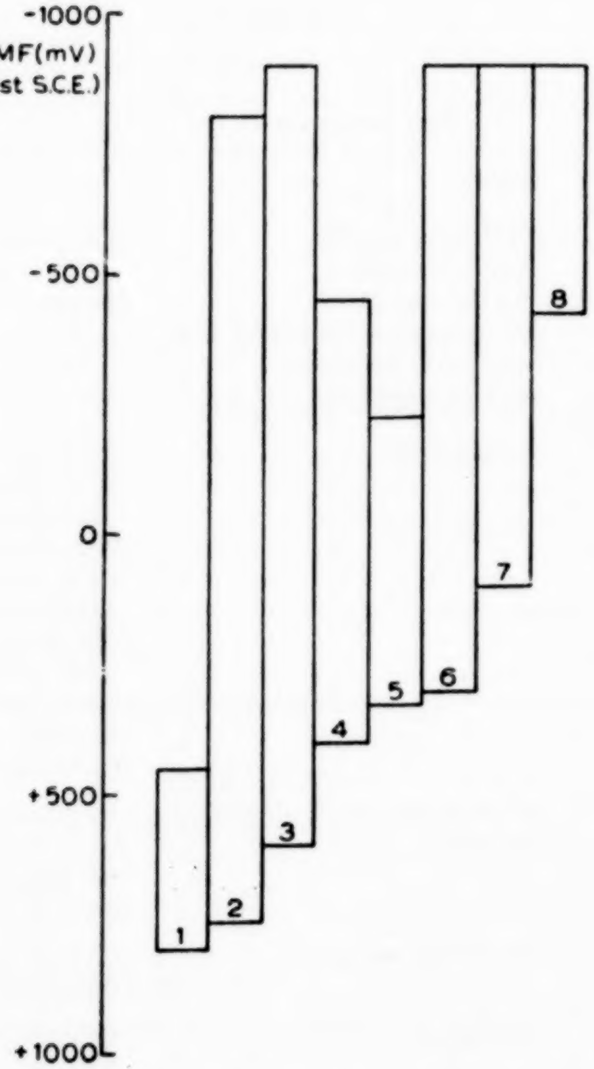

Fig. 1. Acidity potential ranges of eight recommended solvents.

1 = acetic acid
2 = acetone
3 = acetonitrile
4 = *iso*propyl alcohol
5 = water
6 = dimethylformamide (D.M.F.)
7 = pyridine
8 = ethylenediamine (E.D.A.)

TITRANTS

The following facts must be taken into account regarding the solvents for the titrant acids and bases:

In mixtures of solvents, the influence of the most strongly acidic solvent predominates in setting the limit to the acidity potential range on the basic side; the influence of the most basic solvent predominates in setting the limit on the acidic side. A simple schematic illustration of these effects in pyridine and methanol is given in Fig. 2. The effects are especially important in tritations of weak acids, since the most convenient basic titrant solutions contain either water or an alcohol as solvent. However, the presence in the inert or weakly basic solvents, particularly suitable for such titrations, of even a few milliliters of an alcohol added with the titrant may have a decisive influence on the success of the titration.

The choice of the titrant bases is also limited. The use of metal bases such as potassium or sodium hydroxide is restricted by their tendency to form insoluble precipitates in organic solvents.

TABLE I

SOLVENTS

	Type	*Recommended solvent*	*Remarks*
A		*Water*	
B	Alcoholic (weakly acidic, weakly basic)	iso*Propyl alcohol*, Ethyl alcohol, Methyl alcohol (if necessary admixed with non-polar solvents, such as benzene)	These solvents are commercially available in a quality sufficient for use without preliminary purification.
C	Inert (virtually non-acidic, non-basic)	*Acetonitrile*	Acetonitrile may be purified from acetic acid contamination by passage over a column containing a mixture of a strongly basic anion exchange resin in the OH form and a strongly acidic cation exchange resin in the H-form (*e.g.* Amberlite IR 400 and Amberlite IR 120). The first portion of the eluate, which has been used to dispel the water from the column, is discarded. Subsequent portions are distilled before use.
		Acetone (or other aliphatic ketones)	Aliphatic ketones, such as acetone, methylethyl ketone, and *tert.*-butyl methyl ketone, are available in qualities sufficient for use without purification.
		Chlorobenzene	Chlorobenzene may be purified by distillation.
D	Weakly basic (virtually non-acidic)	*Pyridine*	Pyridine is available in a purity sufficient for use without preliminary purification.
		Dimethylformamide	Dimethylformamide should be carefully distilled under reduced pressure.
E	Strongly basic (virtually non-acidic)	*Ethylenediamine* (anhydrous)	Ethylenediamine may be purified[4,5].
F	Strongly acidic (virtually non-basic)	*Acetic acid* (anhydrous)	Acetic acid may be used in analytical grade, with or without admixture of acetic anhydride, depending upon the application[6,7].

The use of sodium hydroxide is moreover limited as a consequence of its interference with the proper functioning of the glass electrode[3]. Tetraalkylammonium bases, on the other hand, which are much more suitable in these respects, are less readily available and considerably more difficult to handle. One of the aims of the tables provided here is to indicate which titrations can be carried out with the simple titrants, and which have to be performed by more elaborate means.

The recommended titrant solutions are listed in Table II, together with indications and references pertaining to their preparation and standardization.

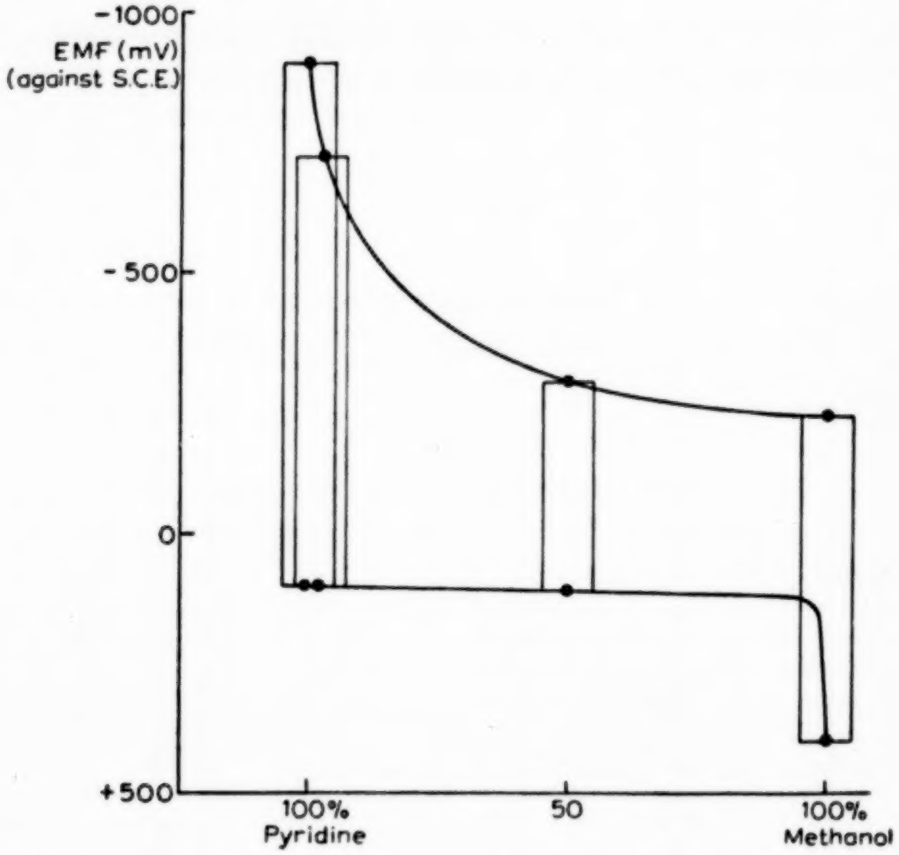

Fig. 2. Schematical representation of acidity potential ranges of mixtures of pyridine and methanol.

TABLE II

TITRANT SOLUTIONS

	Titrant solution	*References*
a	Aqueous alkali	
b	Potassium hydroxide in *iso*propyl alcohol	
c	Tetrabutylammonium hydroxide in *iso*propyl alcohol	DEAL AND WYLD[3]
d	Tetraalkylammonium hydroxide in pyridine	Standardization by titration of a weighed amount of A.G. benzoic acid in pyridine as titration medium: VAN DER HEIJDE AND DAHMEN[1].
e	Piperidine or morpholine in the solvent used as titration medium	Morpholine titrant: CRITCHFIELD AND JOHNSON[8]
f	Perchloric acid in anhydrous acetic acid	FRITZ AND FULDA[6], FRITZ[9]
g	Perchloric acid in dioxane or *p*-toluenesulphonic acid in the solvent used as titration medium	Perchloric acid titrant: FRITZ[10]. Preparation of anhydrous *p*-toluenesulphonic acid: MARYOTT[11]

ACIDS AND BASES TO BE TITRATED

Every acid has a certain "intrinsic" acidity and every base an "intrinsic" basicity that is reflected in their potentials of half neutralizaton (h.n.p.), which are more or less independent of the nature of the solvent.

This value of the h.n.p. cannot, however, be situated outside the acidity range of the solvent in which it is titrated. In this respect, there are four possibilities:

a. If the lower limit of the potential range of the solvent in the titration of acids is higher than the "virtual" h.n.p. of the titrated acid, the latter is levelled up to the former.

b. If the upper limit of the potential range is lower than the virtual h.n.p. of the acid to be titrated, the latter is not neutralized at all, and no titration is possible.

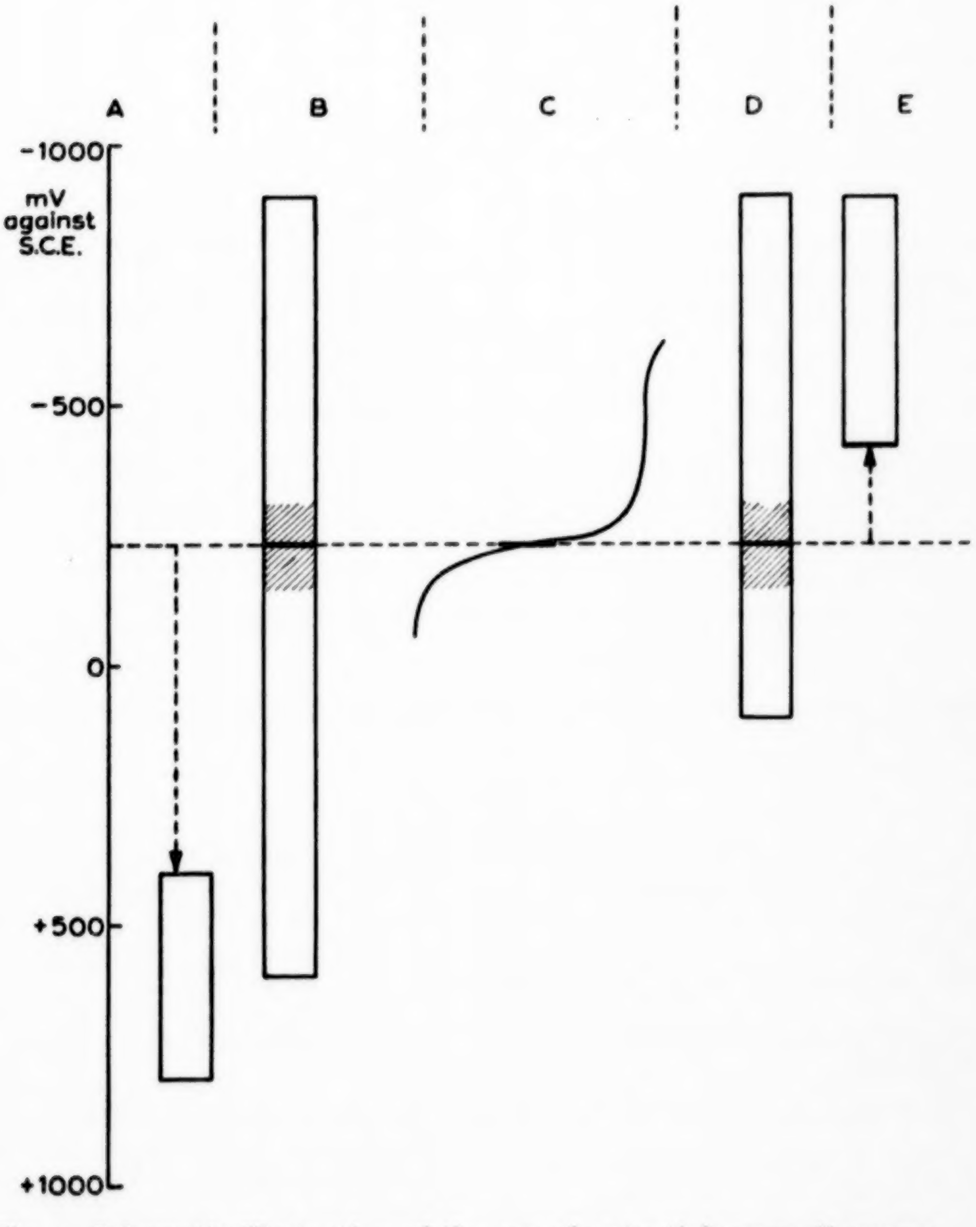

Fig. 3. Schematic illustration of the use of potential range diagrams.

A. Virtual h.n.p. above range of (highly acidic) solvent; no titration possible (case *B*, p. 520).

B. Virtual h.n.p. within range of solvent; actual h.n.p. roughly equal, independent of basicity of solvent.

C. Virtual h.n.p. of acid, reflecting intrinsic acidity.

D. Virtual h.n.p. within range of solvent; actual h.n.p. roughly equal, independent of basicity of solvent.

E. Virtual h.n.p. below range of highly basic solvent; actual h.n.p. is levelled up (case *A*, p. 520).

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c. If the upper limit of the potential range of the solvent in the titration of bases is lower than the virtual h.n.p. of the titrated base, the latter is levelled down to the former.

d. If the lower limit of the potential range of the solvent is higher than the virtual h.n.p. of the titrated base, no titration is possible.

The situation is illustrated in Fig. 3.

The h.n.p. of an acid or base is only related to its "intrinsic" acidity (basicity) if both the titrated substance and its products of neutralization are soluble in the medium.

There are, however, a number of exceptions to this rule that are characteristic for certain types of acids and/or certain types of solvents. These have been dealt with in the previous papers. In the classification of acids presented in Tables III and IV the exceptions have been taken into account.

I. ACIDS

(a) Classification of acids

On the basis of the considerations presented above, the acids have been subdivided according to constitution (first digit), charge type (second digit), and p*K* in water (third digit).

TABLE III

CLASSIFICATION SCHEME FOR ACIDS*

1. *O-Acids*		2. *Non-O-acids and Lewis acids*	
O-Acids contain acid hydrogen bound to oxygen atoms.		Non-O-acids contain their acid hydrogen bound to atoms of other elements than oxygen. Lewis acids are electron-pair acceptors, *i.e.* they derive their acidity not from the capacity to release a proton, but from the capacity to take up a hydroxide (alkoxide, amide, etc.) ion.	
1.1 *Neutral*	1.2 *Negative*	2.1 *Neutral* or	*Positive*
The acid hydrogen is abstracted from an uncharged molecule. Ex.: SO_4H_2, CH_3COOH, C_6H_5OH.	The acid hydrogen is abstracted from a negatively charged ion. Ex.: $KHSO_4$ (SO_4H^-), $R_4NC_2O_4H$ ($C_2O_4H^-$), $CaPO_4H$ (PO_4H^-).	The acid hydrogen is abstracted from an uncharged molecule. Ex.: H_2S, CH_3NO_2, HCl, C_6H_5SH. (Lewis acid): Ex.: CO_2, SO_2, CS_2. Reactions: $CO_2 + OH^- \rightarrow CO_3H^-$.	The acid hydrogen is abstracted from a positively charged ion. Ex.: Ammonium type salts: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$.
↓ In water:	↓ In water:	In water**	
1.1.1 $pK < 2$	1.2.1 $pK < 2$	2.1.1 $pK < 2$	
1.1.2 $2 < pK < 8$	1.2.2 $2 < pK < 8$	2.1.2 $2 < pK < 8$	
1.1.3 $pK > 8$	1.2.3 $pK > 8$	2.1.3 $pK > 8$	

* For the sake of simplicity only those types of acids are included which commonly occur in analytical practice.

** Lewis-type acids are classified according to the p*K* of the corresponding hydrogen acid, which results from reaction with one molecule of water. Example: $pK_{SO_2} = pK_{H_2SO_3}$.

(b) Recommended solvent-titrant combinations for acids

In Tables IV and V the recommended solvent-titrant combinations for titration of acids are given. Table IV applies to the titration of single acids, Table V to the titration of mixtures of acids.

It should be noted that, owing to the enormous diversity of acids and bases, their systematization in Table III is obviously very imperfect.

Consequently, the recommendations should not be assumed to warrant success in every individual case. This is especially true for titrations differentiating among more than one acid in one solution. Success in this case depends not merely upon the relative acid strengths, but also upon the proportion in which they are present in the solution and, of course, upon the desired accuracy.

Under each entry, the recommended solvent-titrant combinations are listed in their order of decreasing convenience of application. The first combination under each entry is the most convenient one that gives a chance of success.

The tables thus render it possible roughly to judge in advance the importance of the considered titration problem against the effort required for preparing the titrant. They further aid in deciding by a minimum number of experiments whether the titration problem can actually be solved by the technique in its present stage of development.

TABLE IV

SOLVENT-TITRANT COMBINATIONS FOR TITRATION OF SINGLE ACIDS

*Type of acid**	*Solvent-titrant combinations***
1.1.1	[A;a], [B;a,b,c], [C;c]
1.1.2	[A;a], [B;a,b c], [D;b,c,d], [E;d]
1.1.3	[D;c,d], [C;c], [E;d]
1.2.1	[A;a], [B;a,b,c]
1.2.2	[A;a], [B;a,b,c], [D;c,d]
1.2.3	—
2.1.1	[A;a], [B;a,b,c], [C;c]
2.1.2	[A;a], [B;a,b,c], [C;c], [D;c,d]
2.1.3	[D;c,d], [C;c,d], [E;d]

* For meaning of digits: see Table III.

** Capital letters indicate solvents (see Table I), small letters indicate titration solutions (see Table II).

II. BASES

The titration of bases in non-aqueous medium is much simpler than the titration of acids. Firstly, the bases most frequently encountered, for which titration in non-aqueous solution is a recommendable procedure, belong without exception to the class of the nitrogen bases. Secondly, the use of strongly acidic titrants in non-basic solvents presents fewer practical difficulties than that of strongly basic titrants in non-acidic solvents.

As a consequence, a large number of these bases can be titrated using only few solvent-titrant combinations[6,7,12].

Solvent-titrant combinations for	
titration of single (N) bases	*differentiating titrations of (N) base-mixtures*
[C;f] [F;f]	[C;g]

Meaning of capital letters: Table I; of small letters: Table II.

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TABLE V

SOLVENT-TITRANT COMBINATIONS FOR DIFFERENTIATING TITRATION OF ACID MIXTURES

Type of acid	1.1.1	1.1.2	1.1.3	1.2.1	1.2.2.	1.2.3	2.1.1	2.1.2	2.1.3
1.1.1	[C;e,c]	[A;a][D;b,c]	[D;c,d]	[B;b,c]	[B;b,c], [C,D;c,d]	—	[C;e,c]	[A;a][C;e,c] [D;b,c]	[D;c,d]
1.1.2	.	[D;b,c,d]	[D;c,d]	[A;a], [D;c,d]	[C;c] [D;c,d]	—	[A;a][C;c] [D;c,d]	[C;c] [D;c,d]	[C;c] [D;c,d]
1.1.3	.	.	[D;d] [E;d]	[D;c,d]	[C;c], [D;c,d]	—	[C;c], [D;c,d]	[C;c] [D;c,d]	[D;d] [E;d]
1.2.1	.	.	.	[B;c] [C;c]	[C;c] [D;c,d]	—	[C;c] [D;c,d]	[A;a],[C;c] [D;c,d]	[C;c] [D;c,d]
1.2.2	.	.	.	.	[C;c] [D;c,d]	—	[C;c] [D;c,d]	[C;c] [D;c,d]	[C;c] [D;c,d]
1.2.3	.	.	.	.	.	—	—	—	—
2.1.1	.	.	.	.	.	.	[C;e,c]	[A;a] [C;c] [D;c,d]	[C;c] [D;c,d]
2.1.2	.	.	.	.	.	.	.	[C;c] [D;c,d]	[C;c] [D;c,d]
2.1.3	.	.	.	.	.	.	.	.	[D;d]

Meaning of digits: see Table III; meaning of capital letters: see Table I; meaning of small letters: see Table II.

EXAMPLES OF THE USE OF THE TABLES

I. Titration of benzoic acid

(1) See Table III:

(a) In benzoic acid the acid proton is bound to oxygen → 1.

(b) The proton is abstracted from a neutral molecule → 1.1.

(c) $pK_{\text{benzoic acid}} = 4.2$ → 1.1.2.

(2) See Table IV: under the entry 1.1.2 we find:

[A; a], [B; a,b,c], [D; b,c,d], [E; d].

(3) See Table I: A = water.

(4) See Table II: a = aqueous alkali.

Thus, benzoic acid is most easily titrated in water with aqueous alkali. Therefore, unless the acid is already present in some non-aqueous solvent, there is no reason to use one for the titration.

II. Titration of p-*phthalic acid*

(1) This acid belongs to the same class as benzoic acid: ($pK \sim 3.5$) → 1.1.2.

(2) The solvent-titrant combinations, [A;a] and [B;a,b,c], are not possible here owing to the insolubility of the acid in water and alcohols.

p-Phthalic acid dissolves easily both in pyridine and in dimethylformamide (D). Upon trial, it will be found that the first of the titrants recommended, KOH in *iso*propyl alcohol (b), cannot be used because of the insolubility of the acid potassium *p*-phthalate in these media. The second titrant recommended, tetrabutylammonium hydroxide in *iso*propyl alcohol (c), will yield satisfactory results, particularly in pyridine as titration medium.

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III. Titration of p-*nitrophenol and nitromethane* if both are present in one solution in methanol (case *A*), or in *iso*propyl alcohol (case *B*), or in ether (case *C*).

(1) See Table III:

p-Nitrophenol is an O-acid → 1.
is neutral → 1.1.
$pK = 7.2$ → 1.1.2.
Nitromethane is a non-O-acid → 2.
is neutral → 2.1.
$pK = 10.2$ → 2.1.3.

(2) See Table V:

On the intersection of the horizontal column marked 1.1.2 and the vertical column marked 2.1.3, we find the solvent-titrant combinations [C;c] and [D;c,d]. According to Tables I and II:

[C;c] : acetonitrile (or aliphatic ketones) as solvent + tetrabutylammonium hydroxide in *iso*propyl alcohol as titrant,

[D;c,d]: pyridine (or dimethylformamide) as solvent + tetrabutylammonium hydroxide in *iso*propyl alcohol or in pyridine as titrant.

From the fact that alcoholic solvents are not recommended here, it may be deduced that neither the solution in methanol (case *A*) nor the solution in *iso*propyl alcohol (case *B*) can be titrated as such to give separate inflections for both acids. Neither will such a titration be feasible if the alcoholic solutions are mixed with the recommended solvents, unless the original solutions are so concentrated that the alcohol content of the solvent mixtures does not exceed 1% of methanol or 10% of *iso*propyl alcohol.

For the same reason the recommended titrant (c), *i.e.* the tetrabutylammonium hydroxide solution in *iso*propyl alcohol will yield a satisfactory inflection for the weaker acid only at low intakes that require small amounts of the titrant. But whenever a small ratio of nitromethane to nitrophenol necessitates a relatively large sample the combination [D;d], *i.e.* pyridine + tetraalkylammonium hydroxide in pyridine, must be chosen.

If the nitrophenol and nitromethane are dissolved in ether (case *C*), the solution may be mixed with the solvent pyridine and can be titrated directly, as ether is inert and does not influence the acidity potential range of pyridine.

Alternately, if the solution in ether is very dilute, the latter may be evaporated from the ether-pyridine mixture prior to titration.

SUMMARY

This paper contains tables and a number of simplified considerations, which will enable the analytical chemist not specialized in the subject to find suitable media for titration in non-aqueous solution of most of the acids and bases commonly encountered in analytical practice. Tables providing guidance in the titration of mixtures of not too closely similar acids or bases are also given. Examples illustrating the application of these tables are included.

RÉSUMÉ

Cette communication contient des tableaux et des considérations simplifiées qui permettront au chimiste analyste non spécialisé dans ce sujet de trouver les conditions appropriées à la titration en solution non-aqueuse des acides et des bases rencontrés ordinairement dans la pratique analytique. Des tableaux fournissant une aide dans la titration de mélanges constitués d'acides ou de bases qui ne se ressemblent pas trop, sont aussi donnés. Des exemples expliquant l'application de ces tableaux sont joints à l'article.

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ZUSAMMENFASSUNG

Diese Arbeit enthält Tabellen sowie einige vereinfachte Betrachtungen, die es dem nicht in diesem Spezialgebiet bewanderten Analytiker ermöglichen, für die Titration in nichtwässriger Lösung der meisten in der analytischen Praxis üblichen Säuren und Basen geeignete Bedingungen zu wählen. Ferner werden Tabellen, die bei dem Titrieren von Mischungen nicht zu ähnlicher Säuren und Basen zum Leitfaden dienen können, sowie Beispiele für die Benutzung dieser Tabellen gegeben.

REFERENCES

[1] H. B. VAN DER HEIJDE AND E. A. M. F. DAHMEN, *Anal. Chim. Acta*, 16 (1957) 378.
[2] H. B. VAN DER HEIJDE, *Anal. Chim. Acta*, 16 (1957) 392.
[3] V. Z. DEAL AND G. WYLD, *Anal. Chem.*, 27 (1955) 47.
[4] G. L. PUTNAM AND K. A. KOBE, *Trans. Electrochem. Soc.*, 74 (1938) 609.
[5] W. H. BROMLEY AND W. F. LUDER, *J. Am. Chem. Soc.*, 66 (1944) 107.
[6] J. S. FRITZ AND M. O. FULDA, *Anal. Chem.*, 25 (1953) 1837.
[7] P. SENSI AND G. G. GALLO, *Ann. chim. (Rome)*, 43 (1953) 453.
[8] F. E. CRITCHFIELD AND J. B. JOHNSON, *Anal. Chem.*, 26 (1954) 1803.
[9] J. S. FRITZ, *Anal. Chem.*, 22 (1950) 1028.
[10] J. S. FRITZ, *Anal. Chem.*, 22 (1950) 578.
[11] A. A. MARYOTT, *J. Research Natl. Bur. Standards*, 38 (1947) 527.
[12] A. F. GREMILLION, *Anal. Chem.*, 27 (1955) 133.

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Note added in proof

It has been mentioned in Part I that the tetraalkylammonium bases used are unstable in pyridine at room temperature. According to C. K. INGOLD (*Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953), substitution of the alkyl chains at the β-position with an electron-donating radical increases the stability towards the bimolecular elimination of olefin. In accordance with these views we have found trimethyl-*iso*butylammonium hydroxide to be completely stable in pyridine at room temperature. As the solvating properties of this particular base may not be sufficient for all purposes it might be profitable to prepare an analogue with more or longer β-ramified alkyl chains.

THE FLAME PHOTOMETRIC DETERMINATION OF CALCIUM IN PHOSPHATE, CARBONATE, AND SILICATE ROCKS

by

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INTRODUCTION

Investigations of the flame photometric determination of calcium have been made on glasses[1], minerals[2], biological materials[3], metallurgical products[4], and water samples[5]. Techniques usually involve either the preliminary separation of calcium from interfering elements, the addition of a saturated solution of a radiation buffer to provide uniform radiation characteristics and minimize the interfering effects of diverse ions, or the comparison of the unknown solution with a standard that incorporates some or all of the interferences present in the unknown solution. In the latter procedure for accurate quantitative analysis the qualitative make-up and approximate quantities of the components present in a given substance must be known.

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* Publication authorized by the Director, U. S. Geological Survey. Present address: New Brunswick Laboratory, U. S. Atomic Energy Commission, P. O. Box 150, New Brunswick, New Jersey.

Our problem was to determine calcium in phosphate, carbonate and silicate rocks containing varying concentrations of the usual rock-forming elements. The method was to be applicable to routine work, and the utmost in accuracy was not required.

Although most elements either enhance or suppress calcium emission to some extent, aluminum and phosphorus cause serious suppression. This effect has been noted by many investigators; MOSHER *et al.* partially overcame the effect of aluminum by the addition of a relatively large amount of magnesium[6]. In the procedure described here the interference is almost entirely overcome by the addition of a large excess of magnesium. The method is applicable to the determination of calcium in the afore-mentioned rock types. Separations are not required and the results are better than ± 2% of the calcium oxide found by gravimetric methods in the 1-95% range. The method compares favorably with standard methods in the 0-1% range, and the lower limit of sensitivity is 0.01%.

This study is part of a program conducted by the Geological Survey on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission.

EXPERIMENTAL DATA

The most sensitive calcium band is at a wavelength of 554 mμ using the blue-sensitive phototube. The oxy-hydrogen flame was selected because of the favorable emission-to-background ratio.

Interference studies were made by adding various amounts of nitric acid to 30 p.p.m. of calcium

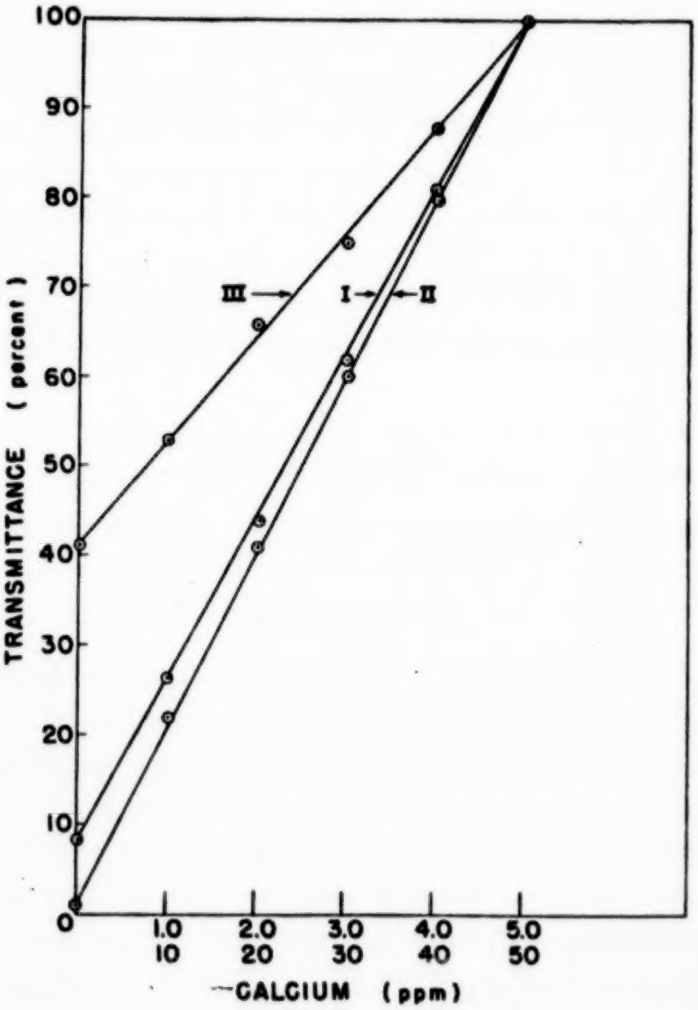

Fig. 1. Standard curves for calcium at 554 mμ.
Curve I: 0-50 p.p.m. Ca + 20 ml radiation buffer; slit width 0.057 mm.
Curve II: 0-50 p.p.m. Ca as NO_3; slit width 0.047 mm.
Curve III: 0-5 p.p.m. Ca + 20 ml radiation buffer; slit width 0.112 mm.

until no further radiation suppression occurred. Next, the effect of perchloric acid increments was tested on 30 p.p.m. of calcium plus the plateau quantity of nitric acid determined in the preceding experiment until another plateau was reached. Succeeding elements were studied in this order: aluminum, phosphoric acid, magnesium, iron, sodium, potassium, and manganese to establish plateau quantities. These experiments determined a radiation buffer containing all the elements that affect calcium emission in such concentrations that suppressing or enhancing effects were overcome. In the procedure developed, the radiation buffer is added to both samples and standards so that the concentration variations within the samples themselves are without effect on the sample emission. The radiation buffer also provides increased flame stability and minimizes drift so common to flame methods. Burner clogging did not occur. The radiation buffer almost completely restores the standard curve obtained from an aqueous solution of calcium nitrate as shown in Fig. 1. Calibration curves for the ranges 0-50 p.p.m. and 0-5 p.p.m. calcium are presented.

Interference studies indicated the following concentration limits for the major rock-forming elements:

Constituent	*mg/100 ml*
Al_2O_3	100
MgO	100
P_2O_5	60
Fe_2O_3	15
Na_2O (no upper limit established)	15
K_2O (no upper limit established)	7
MnO	1.3

Nitric acid and perchloric acid tolerances are 6% v/v and 2.5% v/v respectively.

On the basis of 100 mg of sample made up to 100 ml as described below, the sample can contain 60% P_2O_5, 15% Fe_2O_3, 15% Na_2O, 7% K_2O, and 1.3% MnO. These tolerances permit the analysis of most phosphate, carbonate, and silicate rocks without changing the procedure. Minor rock-forming elements such as chromium, titanium, vanadium, lithium, and barium, unless present as major constituents, do not interfere.

Apparatus

A Beckman model DU spectrophotometer with a model 9220 flame attachment and a model 4300 photomultiplier was used with an oxy-hydrogen flame.

Reagents

Hydrofluoric acid, 48%.

Nitric acid, (1 + 1).

Standard calcium solution (1 ml = 1.00 mg Ca). Dissolve 2.498 g of reagent-grade calcium carbonate dried at 105°C in 10 ml of (1 + 1) nitric acid, transfer to a 1-liter volumetric flask, and dilute to mark with water.

Radiation buffer. Weigh the following into a 400-ml beaker: aluminum metal, foil 0.005 inch, 4.000 g; magnesium ribbon, 9.000 g; iron wire, 0.500 g; sodium nitrate, 2.957 g; potassium nitrate, 0.776 g. Cover with a watch glass, add 100 ml of concentrated nitric acid (add additional nitric acid if necessary), and evaporate to dryness. Dissolve the residue in 1200 ml of (1 + 1) nitric acid and heat to effect solution. Filter through a fine paper if the solution is turbid.

Prepare a standard phosphate solution (1 ml $\sim$ 50 mg phosphorus) by pipetting 22.0 ml of 85% phosphoric acid (sp.gr. 1.69) into a 200-ml volumetric flask and diluting to volume with water. Standardize.

The radiation buffer is prepared by adding a volume of the phosphoric acid solution equivalent to 2.50 g phosphorus to the entire mixed-salt solution and diluting to 2 liters in a volumetric flask.

When a 20-ml aliquot of the buffer is diluted to 100 ml it contains 400 p.p.m. aluminum, 250 p.p.m. phosphorus, 900 p.p.m. magnesium, 50 p.p.m. iron, 80 p.p.m. sodium, 30 p.p.m. potassium, and 6 ml of nitric acid.

Calcium standards equivalent to 50, 40, 30, 20, 10 and 0 p.p.m. are prepared by pipetting 5.00 ml, 4.00 ml, 3.00 ml, 2.00 ml and 1.00 ml of the standard calcium solution into 100-ml volumetric flasks, adding to each 2.5 ml of 75% perchloric acid, 20 ml of the radiation buffer by pipette, and diluting to volume with water.

Procedure

Weigh 0.1000 g of sample into a platinum dish, add 5 ml of (1 + 1) nitric acid, 2.5 ml of 75% perchloric acid, and about 5 ml of 47% hydrofluoric acid. Evaporate on the steam bath until the first fumes of perchloric acid appear, wash down the sides of the dish with water, and again evaporate to the initial appearance of perchloric acid fumes. Repeat with additional nitric and hydrofluoric

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acid if necessary. Add about 20 ml of water and digest on the steam bath to effect complete solution. Transfer to a 100-ml volumetric flask, cool, add by pipette 20 ml of the radiation buffer, and dilute to volume with water.

If the sample is expected to contain over 7% calcium oxide, make an appropriate dilution before adding the radiation buffer so that the calcium concentration is less than 0.05 mg/ml.

If the sample is low in calcium (*i.e.*, < 0.50%), carry a reagent blank along with the sample.

Spectrophotometer settings

Wavelength — 554 mμ,
Sensitivity control — 5 turns from clockwise limit,
Selector switch — 0.1,
Phototube — blue with 22 megohm resistor,
Slit — 0.057 mμ,
Hydrogen — 5 psi,
Oxygen — 10 psi,
Photomultiplier — full sensitivity,
Zero suppression — off.

TABLE I

ANALYTICAL DATA

Sample No.	*Type of sample*	*Calcium oxide content* %	*Calcium oxide found* %
NBS 1A	Limestone	41.32[1]	40.6
NBS 56 B	Phosphate rock	44.06	43.9, 43.7
NBS 79	Fluorspar	94.83	96.6
NBS 80	Soda-limeglass	4.65	4.65
NBS 81	Glass sand	0.029	0.034
NBS 88	Dolomite	30.49	30.6
NBS 91	Opal glass	10.48	10.6, 10.7
NBS 98	Plastic clay	0.21	0.18
NBS 99	Feldspar	0.36	0.38, 0.38
NBS 102	Silica brick	2.29	2.36
NBS 104	Burned magnesite	3.35	3.42
NBS 120	Phosphate rock	49.62	49.4, 49.4
NBS 128	Soda-limeglass	4.76	4.72, 4.75
USGS W-1	Standard diabase	10.95[2]	11.0
USGS G-1	Standard granite	1.35[2]	1.36
1	Brecciated limestone	50.46[3]	50.0
2	Calcareous clay	4.58	4.65
3	Clayey sand	0.48	0.55
4	Conglomeratic limestone	1.80	1.74
5	Apatite	49.50	48.7, 48.5
6	Phosphate rock	1.96	2.02
7	,, ,,	6.01	5.93
8	,, ,,	1.40	1.45
9	,, ,,	22.26	21.95
10	Phosphatic limestone	24.35	24.22
11	Phosphatic clay	0.22	0.23
12	Aluminum phosphate rock[4]	6.9	6.75
13	,, ,, ,,	1.41	1.70
14	,, ,, ,,	11.9	12.1
15	,, ,, ,,	8.6	8.60
16	,, ,, ,,	1.57	1.68

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[1] National Bureau of Standards certificate value.

[2] Average value.

[3] Simple precipitation as oxalate and volumetric determination with potassium permanganate.

[4] Sample 12-16 from the aluminum phosphate zone, Bone Valley formation, of Pliocene age, Florida, usually containing wavellite, crandallite, quartz, and kaolinite.

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Flame photometric procedure

While the 50 p.p.m. calcium solution is aspirating, adjust the wavelength dial to either side of 554 mμ to obtain maximum transmission with a minimum slit width. Adjust the 50 p.p.m. calcium standard to read 100% transmission using the slit width knob. After this adjustment has been made, instrument drift is corrected by minor adjustment of the hydrogen gauge regulator. The sample is then analyzed by bracketing between the closest calcium standards. Three readings are taken on both the sample and the standards and they should agree to ± 1%. Calculations are based on the assumption that the curve is linear between the 10 p.p.m. increment.

After each sample aspirate water through the burner.

SUMMARY

A flame photometric method of determining calcium in phosphate, carbonate, and silicate rocks has been developed. Aluminum and phosphate interference was overcome by the addition of a large excess of magnesium. The method is rapid and suitable for routine analysis. Results obtained are within ± 2% of the calcium oxide content.

RÉSUMÉ

Une méthode photométrique à la flamme, pour la détermination du calcium dans les roches phosphatées, carbonatées et silicatées a été développée. L'interférence de l'aluminium et du phosphate a été évitée par l'addition de magnésium en grand excès. La méthode est rapide et convenable à l'analyse courante. L'erreur dans les résultats est de ± 2% de la teneur en oxyde de calcium.

ZUSAMMENFASSUNG

Eine flammenphotometrische Methode zur Bestimmung von Calcium in Phosphat, Carbonat, und Silikatgesteinen wurde entwickelt. Die Störung von Aluminium und Phosphat wurde überwunden durch Addition grosser Mengen Magnesium. Diese Methode ist schnell auszuführen und wird fur Routine-Analysen empfohlen. Calciumoxyd kann mit einem Fehler von ± 2% bestimmt werden.

REFERENCES

[1] NORMAN RAY, *Anal. Chem.*, 28 (1956) 34.
[2] S. B. KNIGHT, W. C. MATHIS AND J. R. GRAHAM, *Anal. Chem.*, 23 (1951) 1704.
[3] G. R. KINGSLEY AND R. R. SCHAFFERT, *Anal. Chem.*, 25 (1953) 1738.
[4] D. F. KUEMMEL AND H. L. KARL, *Anal. Chem.*, 26 (1954) 386.
[5] P. W. WEST, P. FOLSE AND D. MONTGOMERY, *Anal. Chem.*, 22 (1950) 667.
[6] R. E. MOSHER, E. J. BIRD AND A. J. BOYLE, *Anal. Chem.*, 22 (1950) 715.

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Short Communication

Thermolysis of the molybdenum(VI) 5,7-dibromo-8-quinolinol chelate

One of the methods for the determination of molybdenum(VI) ion is by precipitation as the molybdenum(VI) 8-quinolinol chelate[1]. The precipitation was found to be complete in the pH range of 3.3 to 7.6. In order to carry out the determination in more acid solutions (pH < 1), RAMANA RAO suggested the use of 5,7-dibromo-8-quinolinol as a precipitant[2]. A flocculent, orange-yellow precipitate was obtained which was easy to filter and wash. Since this method appears to be superior to the existing 8-quinolinol method, it was of interest to study the thermal stability of the precipitate on the thermobalance.

The molybdenum 5,7-dibromo-8-quinolinol precipitate was prepared as previously described[2]. The compound was air-dried at room temperature for 24 hours before pyrolysis on the thermobalance. A heating rate of 5.4°C per minute was used.

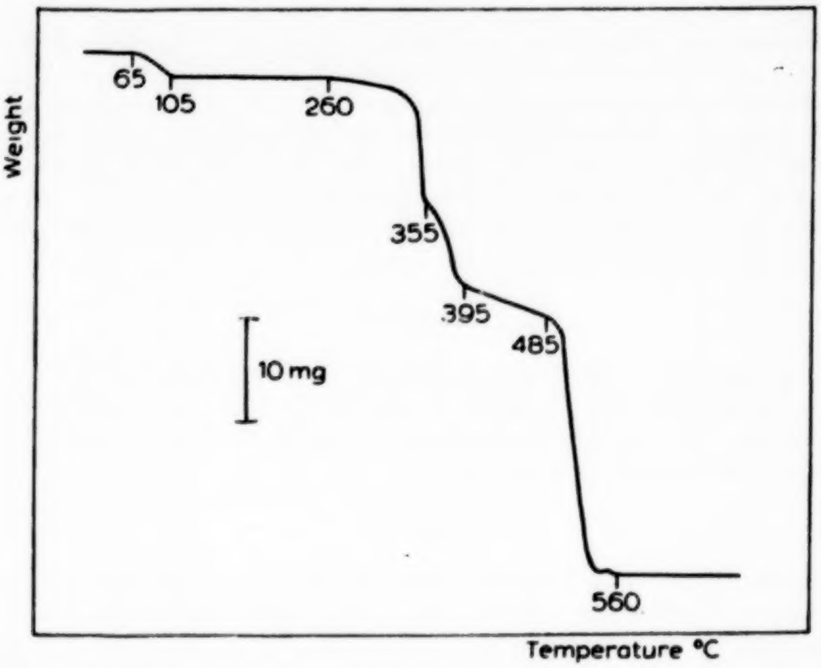

Fig. 1. Thermolysis curve of molybdenum 5,7-dibromo-8-quinolinol chelate.

The thermolysis curve is given in Fig. 1. The precipitated compound corresponded to the formula, $MoO_2(C_9H_4Br_2NO)_2 \cdot \sim 2H_2O$; however, the amount of hydrate water may be fortuitous. Water of hydration began to come off at 65°C, resulting in a horizontal weight level from 105 to 165°C, which corresponded to the anhydrous chelate. Beyond 260°C the compound began to decompose rapidly, giving breaks in the curve at 355 and 395°C. Further decomposition then took place above 485°C to give the MoO_3 level at 560°C.

From the thermolysis curve, it can be seen that the precipitate can easily be weighed as the anhydrous chelate, $MoO_2(C_9H_4Br_2NO)_2$, in the temperature range of 105-260°C. The weighing of the chelate in this form appears to be preferred over that of ignition to MoO_3 because of the possibility of forming the volatile MoO_2Br_2 during the decomposition. This would, of course, give a low oxide content and hence, low results.

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[1] H. GOTO, *J. Chem. Soc. Japan*, 56 (1935) 314.
[2] D. V. RAMANA RAO, *Current Sci. (India)*, 25 (1956) 337.

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DETECTION OF EXHAUSTED COFFEE IN GENUINE ROASTED COFFEE AND ESTIMATION OF THE ADDED AMOUNT

by

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Adulteration of roasted ground coffee by addition of inferior substitutes is ascertained by determination of changes in composition or by specific qualitative reactions, but the best means to detect adulteration is furnished by the microscope. The methods mentioned fail in the case of admixture of exhausted, dried coffee residues. Natural variations in characteristic constituents of ground roasted coffee amount to 20% and more, and are partly influenced by intensity of roasting and by the fineness to which the roasted coffee is ground[1]. Any calculation based on these data must allow for possible wide fluctuations and it is not safe to deduce adulteration by small amounts of exhausted coffee solely from deviations in "normal" composition. Little has been recorded regarding the use of fluorescence analysis in examination of coffee purity. Chicory shows yellowish white fluorescence, while *Taraxacum* root is detected by its blue colour[2]. VALENTIN[3] investigated the application of the chromatographic adsorption method to the differentiation of various kinds of coffee. Filtrates of different starting materials, after running through a column of alumina, gave chromatograms with very similar appearance, except that the violet fluorescence, in ultraviolet light, of malt infusions was weak as compared with that of genuine coffee. The ultraviolet absorption of aqueous extracts of roasted coffee shows two broad absorption bands with maxima at *ca.* 285 mμ and *ca.* 320 mμ. Compounds such as caffeine and furfural have absorption maxima in the 275-285 mμ range while chlorogenic acid is reported to have a maximum at 323 mμ[4]. Measurement of the ultraviolet-absorbing components determined on diluted aqueous extracts[5] showed that a higher extraction of coloured substances — due to increased efficiency of extraction — was obtained with the more finely ground samples. The concentrations of ultraviolet-absorbing components fell with increasing severity of the roast. Under normal brewing conditions, the extracts of coffee beans from different sources show no significant differences in the levels of ultraviolet-absorbing components.

Genuine, ground roasted coffee examined under an ultraviolet lamp shows a bright colour, whereas exhausted, dried residues are dull. But the differences are too small to warrant differentiation and the colour may vary depending on the coffee berry variety and extent of roasting.

The method described in this paper is based on the fact that ground coffee distributed on filter paper shows on extraction with boiling water a brilliant yellowish fluorescence spot surrounding the tested particle, whereas the exhausted particle shows no fluorescence.

MATERIALS AND METHODS

Coffee samples

The origin of the samples used was as follows:

1. African and Brazilian coffee berries - 4 samples.
2. Blended, commercially roasted and ground coffee samples (African and Brazilian), comprising light, medium and heavy roasts - total 45 samples.
3. Coffee substitutes: chicory and roasted cereals - 4 samples.
4. Dry coffee extracts (Nescafé) - 4 samples.
5. Commercially, steam-exhausted, dried coffee residues - 8 samples.

Preparation of extracts on filter paper

The tested substance was distributed on filter paper (Schleicher and Schüll No. 601 or three layers of Whatman No. 1), kept on watch glasses or inverted half Petri dishes (in order to avoid extraction of fluorescing substances from the support). The particles were spotted with boiling water by means of a dropper pipette. Essential requirements for successful application of the test are: scrupulous cleanliness, uniform distribution of coffee particles — in order to eliminate interference from neighbouring particles — and extraction of each particle with water.

Source of illumination

The filter pads to be tested were placed under the rays of an ultraviolet lamp. The tests were made with a Mineralight lamp (type Sl, short wave ultraviolet). Proper lighting is of importance and observation in a darkroom or under a viewing box is recommended.

RESULTS AND DISCUSSION

In the absence of exhausted coffee—or other adulterant—each particle is surrounded by a fluorescing spot. Particles of steam-exhausted coffee residues, obtained from three types of commercial machines, showed no fluorescence. It is understood that absence of fluorescence results from thorough exhaustion of the coffee during commercial processing, and that practically no additional extraction takes place during spotting with hot water. Water-soluble compounds can be completely removed from coffee only by large quantities of water (about 1:130 or more, depending on the size of grains, method of extraction and the proportion between water and coffee)[1]. The extent of extraction of the tested samples is exemplified by the results of the analysis given in Table I.

TABLE I

ANALYSIS OF ORIGINAL AND EXHAUSTED COFFEE SAMPLES*

		Total ash (%)	*Caffeine* (%)	*Water-soluble matter* (%)
I	1 Original coffee	4.88	2.00	28.6
	2 Exhausted	1.61	0.13	6.1
	3 Exhausted	1.50	0.13	4.1
II	4 Original	4.84	2.06	29.2
	5 Exhausted	1.53	0.22	6.2
	6 Exhausted	1.53	0.27	7.4
III	7 Original	5.01	2.25	28.3
	8 Exhausted	1.68	0.17	4.4
	9 Exhausted	2.27	0.12	4.2
IV	10 Original	4.59	2.15	27.4
	11 Exhausted	1.49	0.14	5.4
	12 Exhausted	1.45	0.13	5.3

* All figures expressed on dry matter basis.
The original coffee was of African source.

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The typical fluorescence seems to be evoked by substances originally present in raw coffee and not by those formed during roasting, since the yellowish spot was also observed on testing extracted (on filter paper) raw coffee particles. The spot was also obtained on testing ground, roasted coffee samples stored up to three years in paper bags.

The method enabled us to ascertain the presence of minute amounts of exhausted coffee added to genuine coffee. A rough approximation of the amount of the adulterant in a suspected sample can be obtained by comparison with controls of known composition. The procedure needs some experience and caution as the fluorescing flecks stand out in the tested field and there is a tendency to overestimate the amount of genuine coffee. For the sake of comparison it is suggested that always the same amount of tested material should be used (*i.e.* 10 mg on a filter pad of 50 square inches area). The amount of adulterant can be estimated by counting the fluorescing flecks and particles showing no halo of fluorescence. Examination and comparison of filter pads can be made immediately after spotting with hot water, but better results are obtained after the pads have dried. No change in appearance of dry pads was observed on careful storing for several months. On comparison of filter pads it is assumed that the particle size distribution of the genuine and exhausted coffee is equal.

Chicory particles appeared on testing as brownish particles surrounded by a spot of the same colour; coffee substitutes based on cereals were characterized by a brown yellowish fluorescence. The test can therefore be extended and used for the general examination of coffee purity.

ACKNOWLEDGEMENT

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SUMMARY

A method for the detection and estimation of the percentage of exhausted coffee admixed to genuine coffee is presented. The method is based on a fluorescence spot test obtained on water extraction of the tested substance spread on filter paper. The use of the proposed test for general examination of coffee purity is discussed.

RÉSUMÉ

On présente une méthode de détection et d'estimation en % de l'extrait de café (par exemple Nescafé) mélangé au café naturel. La méthode est basée sur un spot-test de fluorescence du produit d'extraction par l'eau de la substance examinée, répandue sur du papier-filtre. On envisage l'utilisation de cette méthode pour la détermination générale de la pureté du café.

ZUSAMMENFASSUNG

Eine Methode zum Nachweis und zur Bestimmung des Gehaltes (in Prozenten) von erschöpftem Kaffee welcher dem natürlichen Kaffee beigemischt ist, wird beschrieben. Die Methode gründet sich auf eine Fluoreszenz-Tüpfelprobe welche man ausführt indem man die zu prüfende auf Filtrierpapier ausgebreitete Substanz mit Wasser extrahiert. Die Anwendung der vorgeschlagenen Probe zur allgemeinen Prüfung des Reinheitsgrades von Kaffee wird erörtert.

REFERENCES

[1] H. THALER, *Deut. Lebensm.-Rundschau*, 51 (1955) 283.
[2] R. VASICKY, *Pharm. Post*, 46 (1913) 877.
[3] H. VALENTIN, *Pharm. Ztg.*, 82 (1937) 527.
[4] B. E. PROCTOR AND S. E. GOLDBLITH, in E. M. MARK AND G. F. STEWART, *Advances in Food Research*, Vol. III, Academic Press, Inc., New York, 1951.
[5] A. C. LITTLE AND G. MACKINNEY, *Food Technol.*, 10 (1956) 503.

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SUR UNE CAUSE D'ERREUR DANS LE DOSAGE PAR VOIE HUMIDE DE L'AZOTE DANS LES ACIERS SPECIAUX

par

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L'aptitude à l'emploi des acides forts (acides chlorhydrique ou sulfurique) pour le dosage de l'azote dans les aciers ordinaires et spéciaux par la méthode de Kjeldahl est généralement éprouvée au moyen d'essais à blanc conduits parallèlement à l'analyse, au moyen des mêmes réactifs. Selon la teneur moyenne d'azote à déterminer, et la précision désirée, on estime en général satisfaisants les acides dont l'essai à blanc ne dépasse pas 0.001 à 0.002% N_2.

Utilisant des lots d'acide chlorhydrique spécifiés „pour analyse" ainsi contrôlés, nous nous sommes aperçus qu'alors que certains aciers non alliés donnaient des valeurs convenablement reproductibles pour leur teneur en azote, certains aciers alliés analysés en même temps donnaient des chiffres très dispersés et le plus souvent notablement supérieurs à ceux obtenus par une autre méthode de référence, telle que la fusion réductrice dans le vide.

Nous avons pensé que cette anomalie provenait d'une impureté de l'acide génératrice d'ammoniaque et non mise en évidence par l'essai à blanc.

Par ailleurs, il avait été observé que les anomalies les plus marquées étaient obtenues quand l'acier analysé contenait du molybdène. Afin d'éclairer la cause de ces anomalies, les séries d'essais ci-après ont été exécutées:

1ère série d'essais. Lot d'acide chlorhydrique A

On a opéré sur deux aciers de composition suivante:

Acier CF: C = 0.05; Si = 0.26; Mn = 0.27; Mo = 0.030. Les traces de molybdène contenues dans cet acier n'étaient pas intentionnelles.

Acier GMa: C = 0.11; Si = 0.24; Mn = 0.67; Ni = 1.42; Cr = 1,08; Mo = 0.150.

Afin de voir si l'impureté supposée était distillable ou non, des analyses ont également été faites en utilisant l'acide du lot A après distillation, et ramené à la même densité (*d* = 1.17 - 1.19).

Les résultats suivants ont été obtenus (l'essai à blanc était dans les deux cas de l'ordre de 0.001 et a été déduit).

TABLEAU I

	Attaque:	
	HCl distillé	*HCl non distillé*
CF	0.011	0.010
GMa	0.013	0.019

L'impureté perturbatrice subsiste donc dans le résidu non distillé, et il se confirme que l'acier non allié n'est pas sensible à son influence.

2ème et 3ème série d'essais. Lot d'acide chlorhydrique A

Dans la seconde série, il a été répété les essais de la précédente et en outre ajouté à l'acier CF, après mise en solution chlorhydrique, séparément ou à la fois les constituants spéciaux de l'acier GM (nickel, chrome et molybdène métalliques), sensiblement aux mêmes teneurs:

TABLEAU II

	Attaque:	
	HCl distillé	*HCl non distillé*
CF	0.010	0.010
GMa	0.013	0.020
CF + 1.3 % Ni	0.011	0.011
CF + 1.0 % Cr	0.011	0.011
CF + 0.2 % Mo	0.011	0.017
CF + (1.5 Ni + 1.0 % Cr + 2 % Mo)	0.011	0.017

Il se confirme donc que l'élément responsable de la „sensibilisation" de l'impureté de l'acide, dans le lot en question, est bien le molybdène.

Une troisième série d'aciers contenant diverses teneurs en molybdène a été alors analysée dans les mêmes conditions et a donné les résultats reportés au Tableau III.

TABLEAU III

		Attaque:	
	Mo %	*HCl distillé*	*HCl non distillé*
CF	0.030	0.011	0.010
GMb	0.150	0.013	0.020
Ga	0.055	0.014	0.020
Gb	0.050	0.016	0.019
GMc	0.222	0.016	0.020
GMd	0.240	0.013	0.020
Va	0.240	0.013	0.019
Vb	0.300	0.013	0.019

Les aciers de la série G étaient des aciers au nickel-chrome du type 16 NC 6 au nickel-chrome, ceux de la série GM du type 14 NCD 6 au nickel-chrome molybdène, et ceux de la série V du type 35 CD 4 au chrome-molybdène. Il semble donc que dans les aciers alliés commerciaux qui peuvent contenir des traces de molybdène ce dernier élément continue à jouer son rôle en présence d'acide impur. Le seuil de la teneur en molybdène active se situerait, dans le cas du lot d'acide A, entre 0.030 et 0.050.

4ème série d'essais. Lot d'acide chlorhydrique A

Pour préciser à partir de quelle teneur le molybdène est susceptible de perturber le dosage de l'azote en présence d'acide impur, nous avons repris, cette fois uniquement avec l'acide non distillé, les essais d'addition de teneurs croissantes de molybdène métallique à un acier de base n'en contenant pas. Les résultats sont donnés au Tableau IV:

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TABLEAU IV

		Attaque:
		HCl non distillé
CF	contenant 0.30 % Mo	0.011 — 0.011
CF + 0.010 % Mo	soit 0.040 % Mo total	0.015 — 0.016
,, + 0.020 ,,	,, 0.050 % ,, ,,	0.012 — 0.014
,, + 0.030 ,,	,, 0.060 % ,, ,,	0.013 — 0.016
,, + 0.050 ,,	,, 0.080 % ,, ,,	0.014 — 0.018
,, + 0.100 ,,	,, 0.130 % ,, ,,	0.015 — 0.018
,, + 0.200 ,,	,, 0.230 % ,, ,,	0.017 — 0.020
,, + 0.400 ,,	,, 0.430 % ,, ,,	0.017 — 0.018
,, + 0.800 ,,	,, 0.830 % ,, ,,	0.016 — 0.018

Ces essais confirment que l'effet perturbateur est obtenu entre 0.030 et 0.40% Mo dans la liqueur d'attaque et que cet effet n'augmente pas ensuite d'une façon très marquée pour des teneurs en molybdène croissantes, ce qui fait penser à une action de caractère catalytique.

5ème série d'essais. Lot d'acide chlorhydrique B

Un second lot d'acide chlorhydrique, repéré pour donner des anomalies encore plus importantes que le précédent, a également été essayé dans les mêmes conditions. Aussi bien non distillé que distillé, cet acide donnait un essai à blanc de 0.001% N_2.

Les aciers, en dehors des aciers CF et CMa des essais précédents, ont été 3 aciers inoxydables (ZM) au nickel-chrome molybdène type 18/10 Mo et un acier inoxydable au nickel-chrome (Z) type 12/12 sans molybdène:

TABLEAU V

	Attaque:	
	HCl distillé	*HCl non distillé*
CF	0.010	0.025
GMa	0.013	0.064
ZMa (avec Mo)	0.035	0.085
ZMb (,, ,,)	0.034	0.083
ZMc (,, ,,)	0.033	0.082
Z (sans Mo)	0.024	0.025

On voit ici que même l'acier CF, à 0.030% Mo, présente l'anomalie de dosage avec le lot d'acide B apparemment plus impur que le lot A. La teneur en molybdène limite perturbatrice doit donc être d'autant plus basse que l'acide est plus impur.

Dans cette même série d'essais, nous avons enfin dosé l'azote dans un échantillon de fer électrolytique, en l'absence et en présence de molybdène. Les chiffres trouvés ont été les suivants:

TABLEAU VI

	Attaque:	
	HCl distillé	*HCl non distillé*
Fer électrolytique	0.003	0.005
,, ,, + 0.2 % Mo	0.003	0.046

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Ceci confirme l'apport parasite de 0.040 à 0.050% N_2 apporté par l'acide impur. Toutefois l'addition de molybdène seul à l'essai à blanc n'a pas modifié ce dernier qui est resté de l'ordre de 0.001% N_2. La présence de fer est donc nécessaire; nous reviendrons plus loin sur cette remarque.

Essai d'identification des impuretés

La présence dans l'acide de sels d'ammonium, qui distilleraient dans tous les cas, étant exclue, nous avons essayé de caractériser dans l'acide chlorhydrique la présence de nitrites ou de nitrates. La réaction des nitrites avec le réactif de Griess[1] a toujours été négative; par contre, avec le réactif de Granval et Lajoux[2] nous avons pu déceler la présence de nitrates. Il a été procédé au dosage des nitrates par la méthode de réduction par l'alliage de Devarda[3] en milieu alcalin suivi de la distillation et du dosage habituel de l'azote, après avoir vérifié avec des additions connues de nitrate que la méthode était quantitative. En raison des faibles teneurs totales en nitrates, les résultats ont été relativement inconstants, la méthode utilisant l'alliage de Devarda s'appliquant généralement à des teneurs en nitrates très supérieures. Afin de caractériser la teneur en azote de l'acide, il paraît donc plus certain d'opérer avec un échantillon de fer électrolytique à teneur en azote très basse et connue et avec addition de molybdène. On a noté que l'addition de molybdène seul à l'essai à blanc conduit au moyen de l'acide impur n'a pas modifié le résultat de cet essai, qui est resté faible ou nul (< 0.001). On retrouve là un fait déjà signalé dans un procédé de dosage des nitrates par KOLTHOFF, SANDELL ET MOSKOVITZ[4]: on effectue la réduction par une solution de fer ferreux titrée, la réaction étant catalysée par addition de molybdate d'ammoniaque.

CONCLUSIONS ET RÉSUMÉ

Le dosage de l'azote dans les aciers ordinaires ou spéciaux par la méthode de Kjeldahl peut être entaché d'erreur par excès si l'acide servant à mettre l'acier en solution, même réputé „pro analysi", contient des impuretés telles que des nitrates, et si le métal luimême présente des teneurs même négligeables (quelques dix millièmes) de molybdène. L'essai à blanc peut dans ce cas malgré cela être très faible ou nul.

Afin de caractériser à ce point de vue la qualité de l'acide employé, il est nécessaire de comparer les teneurs d'azote obtenues sur un échantillon à très basse teneur en azote, par exemple le fer électrolytique, respectivement en l'absence et en présence d'une faible addition (0.1% environ) de molybdène, les différences entre ces déterminations doivent être négligeables. Sinon l'acide essayé doit être rejeté, ou bien distillé avant emploi.

SUMMARY

The estimation of nitrogen in normal or special steels by the Kjeldahl method can give results that are too high if the acid used to dissolve the steel (even "pro analysi" acid) contains impurities such as nitrates, and if the metal itself contains even negligible amounts of molybdenum (*e.g.* a few ten-thousandths). In this case the blank test can nevertheless give a very weak or negative result.

In order to ascertain from this point of view the quality of the acid used, it is necessary to compare the nitrogen contents obtained on a sample with a very low nitrogen content, *e.g.* electrolytic iron, in the absence or in the presence, respectively, of a minute addition (about 0.1%) of molybdenum. The difference between these determinations should be negligible. If it is not, then the acid tested should be rejected, or distilled before use.

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ZUSAMMENFASSUNG

Die Bestimmung von Stickstoff in gewöhnlichen und besonderen Stählen nach der Kjeldahl'schen Methode kann zu hohe Resultate ergeben wenn die zur Auflösung des Stahls verwendete Säure (auch eine sogenannte „pro analysi" Säure) Verunreinigungen wie Nitrate enthält und wenn das Metall selbst auch nur Spuren (einige Zehntausendstel) von Molybdän enthält. Der Blindversuch kann trotzdem in diesem Fall einen sehr schwachen oder einen Nullwert ergeben.

Um die Qualität der Säure in dieser Beziehung zu charakterisieren muss man die für eine Probe mit sehr geringem Stickstoffgehalt (z.B. elektrolytisches Eisen) erhaltenen Stickstoffgehalte, resp. in Abwesenheit und in Gegenwart einer kleinen Molybdänmenge (ungefähr 0.1%) mit einander vergleichen; die Unterschiede zwischen den Ergebnissen dieser Bestimmungen müssen vernachlässigbar sein, sonst muss die untersuchte Säure verworfen oder vor Verwendung destilliert werden.

BIBLIOGRAPHIE

[1] G. CHARLOT ET D. BÉZIER, *Analyse quantitative minérale*, 3e Ed., Masson & Cie., Paris 1955, p. 411.

[2] G. CHARLOT ET D. BÉZIER, *ibid.*, p.414.

[3] G. CHARLOT ET D. BÉZIER, *ibid.*, p. 411.

[4] I. M. KOLTHOFF, E. B. SANDELL ET B. MOSKOVITZ, *J. Am. Chem. Soc.*, 55 (1933) 1454.

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APPLICATION DE LA CHÉLATOMÉTRIE AU DOSAGE DES ESTERS ET CHLORURES DE MONO-ESTERS OXALIQUES

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PRINCIPE

Les esters oxaliques sont facilement et quantitativement saponifiés à chaud par la soude alcoolique pour donner de l'oxalate de sodium accompagné des sels de sodium provenant de la décomposition des impuretés présentes dans l'échantillon examiné et parmi lesquelles on peut retrouver notamment les formiates qui se forment presque toujours dans l'estérification de l'acide oxalique[1]; la saponification des chlorures de mono-esters oxaliques fournit en outre du chlorure de sodium; celui-ci ne provient d'ailleurs pas seulement du chlorure d'acyle examiné mais aussi des différents produits chlorés formés dans sa préparation[2,3,4] ou par décomposition pendant sa distillation[5] tels que oxychlorure de carbone (phosgène), chloroformiates, chlorures d'alcoyle, etc. (nous avons observé que les plus volatils de ces corps étaient facilement et fortement retenus en solution dans les chlorures que nous avons étudiés).

Dans ces conditions, il est bien évident que ni l'indice de saponification ni le taux de chlore ne peuvent servir de base pour l'établissement du titre de ces substances. La détermination de l'anion oxalique après saponification, par les méthodes manganimétriques en milieu acide[6] est également mise en défaut en présence de formiates qui sont, bien que plus lentement que les oxalates, oxydés par le permanganate de potassium[7]; la présence de l'anion chlorhydrique peut perturber ce dosage qui est d'autre part, complètement faussé par le sulfite de sodium provenant du chlorure de

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thionyle pouvant rester dans les chlorures de mono-esters préparés suivant le procédé décrit par Diels et Nawiasky[2].

On sait que l'oxalate de calcium peut être précipité quantitativement[8] et que cette propriété, si on prend la précaution d'éviter la précipitation du carbonate de calcium en chassant par ébullition le gaz carbonique contenu dans l'eau et les solutions aqueuses utilisées, peut être mise à profit pour doser l'acide oxalique et les oxalates alcalins par gravimétrie[9]; mais les lavages et la calcination que nécessite cette méthode la rendent particulièrement peu pratique en regard des possibilités qu'offre la volumétrie.

Les méthodes volumétriques passant par le sel de calcium consistent, après filtration et lavages, à redissoudre le précipité dans un acide fort et à titrer les anions oxaliques dans la solution par cérimétrie ou manganimétrie[10] directement ou par retour au moyen d'un sel ferreux; nous avons trouvé plus simple d'utiliser une solution de chlorure de calcium de titre connu et, après élimination de l'oxalate de calcium par filtration, de mesurer directement l'excès de calcium dans le filtrat au moyen de l'éthylène-diaminotétracétate disodique[11,12]; le sulfite de sodium ou les phosphates mono- et disodiques formés dans la saponification et pouvant provenir du chlorure de thionyle d'après le procédé Diels et Nawiasky[2] ou de l'oxychlorure de phosphore d'après les autres procédés[3,4] ne gênent pas s'ils sont en faible quantité et dans les conditions de précipitation que nous indiquons ci-après car les sels de calcium correspondants sont légèrement solubles dans l'eau au pH auquel nous opérons.

PARTIE EXPÉRIMENTALE

Réactifs utilisés :

Acide acétique
Noir Eriochrome à 0.2%
Réactif Magnésien
Chélate disodique M/50
Chlorure de calcium M/5

Ces réactifs sont les mêmes que ceux que nous avons utilisés dans notre technique de dosage du *fluor* dans les composés organiques[13].

Solution alcoolique de soude N. Nous avons préparé cette solution par simple mélange d'une lessive de soude caustique et d'alcool éthylique en proportion calculée de façon à obtenir une concentration voisine de la normalité (conserver en flacon bien bouché).

Acétate de sodium M. Cette solution est obtenue par la dissolution de 136 g d'acétate de sodium cristallisé (3aq.) dans 800 ml d'eau distillée fraîchement boullie; on étend ensuite à un litre avec cette même eau.

Mode opératoire

On pèse un poids *p* de la substance étudiée* qu'on place dans un ballon à saponification à col rodé, ajoute 10 ml de solution alcoolique de soude *N***, place un réfrigérant ou tube de verre sur le col et porte au bain-marie bouillant pendant une heure; on refroidit, ajoute 10 ml d'acide acétique et transvase dans une fiole jaugée en Pyrex de 250 ml en rinçant plusieurs fois à l'eau distillée; on porte à ébullition pendant quelques minutes pour chasser le gaz carbonique; on ajoute 50 ml d'acétate de sodium M, puis, en maintenant toujours l'ébullition, 25 ml de chlorure de calcium $M/5$ exactement mesurés; on refroidit à température ambiante et complète à 250 ml au moyen d'eau distillée fraîchement bouillie; on filtre rapidement et prélève, au moyen d'une pipette, 25 ml de filtrat auxquels on ajoute 10 ml de Réactif Magnésien exactement mesurés et quelques gouttes de Noir Eriochrome à 0.02%; on chauffe vers 50°C et coule le chélate disodique $M/50$ au moyen d'une burette jusqu'au virage du rouge au bleu; ce virage est net mais assez lent à se produire et il y a lieu d'opérer lentement en fin de dosage; le titre % du composé oxalique étudié est donné par la formule:

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* On calcule *p* de façon qu'il contienne environ 0.002 molécule-gramme.

** Les chlorures de mono-esters oxaliques réagissent énergiquement sur la soude; pour éviter les pertes de substance par évaporation au moment de la réaction, nous avons employé le dispositif suivant: une cupule de verre est posée au fond du ballon à saponification choisi à fond plat; on tare le tout et pèse la substance dans la cupule; on introduit alors, au moyen d'une pipette, la soude alcoolique autour de la cupule puis place, sur le col du ballon, le tube rodé après l'avoir mouillé intérieurement avec 2 à 3 ml de soude alcoolique et muni au sommet d'un tampon d'ouate de verre également imbibé de ce réactif; on agite alors le tout pour renverser la cupule.

Après saponification, on rince le tampon et le tube par un jet d'eau distillée.

$$T = \frac{M \times V}{p}$$

$V \quad = 2.5\, N_{K}' - V'\, N_{c}'$;
N_{K}' = normalité de la solution de chlorure de calcium;
V' = nombre de ml de chélate utilisé;
N_{c}' = normalité du chélate.
M = masse moléculaire du corps dosé.

RÉSULTATS OBTENUS

Nous avons essayé la présente technique sur divers composés oxaliques très soigneusement rectifiés; nous résumons dans le Tableau I les résultats que nous avons obtenus.

TABLEAU I

Nature	*Poids*	*Titre trouvé*
Oxalate de méthyle	0.237	100.2
	0.244	100.3
Oxalate d'éthyle	0.307	100.3
	0.301	100.1
Oxalate de propyle	0.354	99.6
	0.347	99.4
Oxalate d'*iso*propyle	0.351	99.6
	0.357	99.6
Oxalate de butyle	0.402	99.0
	0.397	99.2
Oxalate d'*iso*butyle	0.398	99.4
	0.405	99.3
Oxalate de butyle$_2$	0.402	99.5
	0.391	99.4
Oxalate d'allyle	0.352	99.6
	0.359	99.8
Oxalate d'éthyle (90%), formiate d'éthyle (10%)	0.327	90.2
	0.322	90.1
Oxalate de propyle (90%), formiate de propyle (10%)	0.384	90.0
	0.379	89.8
Chlorure de méthoxalyle *	0.241	99.4
	0.253	99.5
Chlorure d'éthoxalyle **	0.283	99.6
	0.277	99.3
Chlorure d'éthoxalyle (+ 5 mg $SOCl_2$)	0.289	99.7
	0.274	99.5
Chlorure d'éthoxalyle (+ 5 mg $POCl_3$)	0.282	99.4
	0.289	99.7

* Teneur en chlore = 29.15; teneur théorique = 28.94.
** Teneur en chlore = 26.12; teneur théorique = 25.97.

RÉSUMÉ

Les esters et les chlorures des mono-esters oxaliques peuvent être dosés volumétriquement, après saponification, par précipitation au moyen d'une solution de chlorure de calcium dont on mesure l'excès par chélatométrie.

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SUMMARY

Esters and chlorides of oxalic mono-esters can be estimated volumetrically. After saponification precipitation is carried out by means of a calcium chloride solution, the excess of which is measured by chelatometry.

ZUSAMMENFASSUNG

Die Oxalsäureester und Chloride der Oxalsäure-Monoester können volumetrisch bestimmt werden. Nach Verseifung fällt man mit einer Calciumchloridlösung deren Überschuss chelatometrisch bestimmt wird.

BIBLIOGRAPHIE

[1] V. Grignard, G. Dupont et R. Locquin, *Traité de chimie organique*, Masson & Cie., Paris, 1939, Tome X, p. 171.
[2] O. Diels et P. Nawiasky, *Ber.*, 37 (1904) 3678.
[3] L. Henry, *Ber.*, 4 (1871) 598.
[4] V. von Richter, *Ber.*, 10 (1877) 2229.
R. Anschütz, *Ber.*, 19 (1886) 2159.
R. Anschütz, *Ann.*, 254 (1889) 1.
A. Peratoner et B. Strazzeri, *Gazz. chim. ital.*, 21 (1891) 300.
D. Mol, *Rec. trav. chim.*, 26 (1907) 373.
R. Scholl et W. Egerer, *Ann.*, 397 (1913) 301.
[5] G. Grassi-Cristaldi, *Gazz. chim. ital.*, 27 I (1897) 32.
[6] A. Skrabal, *Z. anorg. Chem.*, 42 (1904) 1.
A. Skrabal, *Z. Elektrochem.*, 11 (1905) 653.
F. P. Treadwell, W. D. Treadwell et M. Boll, *Manuel de chimie analytique*, Tome 2, Dunod, Paris, 1948, p. 556.
A. Boutaric, *Compt. rend.*, 160 (1915) 711.
[7] A. Skrabal et J. Preiss, *Monatsh. Chem.*, 27 (1906) 503.
J. Holluta, *Z. physik. Chem.*, 101 (1922) 34, 489.
[8] I. M. Kolthoff et E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, McMillan Co., New-York, 1952.
J. Haslam, *Analyst*, 60 (1935) 668.
[9] D. Mol, *Rec. trav. chim.*, 26 (1907) 373
M. Boll et J. Leroide, *Précis d'analyse chimique*, Tome 3, Dunod, Paris, 1929, p. 179.
F. P. Treadwell, W. D. Treadwell et M. Boll, *Manuel de chimie analytique*, Tome 2, Dunod, Paris, 1948, p. 72.
[10] M. Boll et J. Leroide, *Précis d'analyse chimique*, Tome 2, Dunod, Paris, 1927, p. 92.
J. B. McNair, *J. Am. Chem. Soc.*, 54 (1932) 3249.
R. Linder et P. L. Kirk, *Mikrochemie*, 22 (1937) 291.
G. H. Ellis, *Ind. Eng. Chem., Anal. Ed.*, 10 (1938) 112.
P. L. Kirk et P. C. Tompkins, *Ind. Eng. Chem., Anal. Ed.*, 13 (1941) 277.
F. P. Treadwell, W. D. Treadwell et M. Boll, *Manuel de chimie analytique*, Tome 2, Dunod, Paris, 1948, p. 573.
G. Charlot et D. Bézier, *Méthodes modernes d'analyse quantitative minérale*, Masson & Cie., Paris, 1949, p. 355, 358.
[11] G. Schwarzenbach et W. Biedermann, *Chimia*, (*Switz.*), 2 (1948) 56.
H. Diehl, C. A. Goetz et C. C. Hach, *J. Am. Water Works Assoc.*, 42 (1950) 40.
E. Leroi et J. A. Gautier, *Ann. pharm. franç.*, 11 (1953) 329.
G. Schwarzenbach, *Die komplexometrische Titration*, Ferd. Enke, Stuttgart, 1955.
[12] W. Biedermann et G. Schwarzenbach, *Chimia* (*Switz.*), 2 (1948) 1.
J. D. Betz et C. A. Noll, *J. Am. Water Works Assoc.*, 42 (1950) 49.
J. J. Conners, *J. Am. Water Works Assoc.*, 42 (1950) 33.
C. A. Goetz, T. C. Loomis et H. Diehl, *Anal. Chem.*, 22 (1950) 798.
K. Knie, *Österr. Wasserwirtsch.*, 4 (1952) 13.
G. R. Botha et M. M. Webb, *J. Inst. Water Engrs.*, 6 (1952) 459.
J. Banks, *Analyst*, 77 (1952) 484.
M. Brooke et M. Holbrook, *Chemist Analyst*, 41 (1952) 80.
P. Souchay et M. Craizon, *Bull. soc. chim. France*, (1952) 34.
S. I. Sinjakova, *Zhur. Anal. Khim.*, 10 (1955) 139.
A. Baroccio et C. Nigro, *Ann. sper. agrar.* (*Rome*), 10 (1956) 119.
J. Patton et W. Reeder, *Anal. Chem.*, 28 (1956) 1926.
M. Friedrich et M. Fáborský, *Sklář a keram.*, 6 (1956) 114.
Z. Host'ialek et M. Pollertova, *Chem. průmysl*, 6 (1956) 271.
J. Krizova, *Stavivo*, 34 (1956) 239.
[13] C. Hennart et E. Merlin, *Anal. Chim. Acta*, 17 (1957) 463.

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OXINE COMPLEX OF MOLYBDENUM

by

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INTRODUCTION

Several organic reagents are employed to precipitate metals and for a particular element to be precipitated in the presence of other potentially interfering elements, selectivity may be achieved in two ways: some other reagent that forms a complex and slightly dissociated ion with the other interfering elements may be used or the pH of the solution may be so controlled as to make the condition not favourable for the precipitation of other elements. The recent work along these lines reveals the utilisation of either of these two methods. Molybdenum was reported[1] to be precipitated quantitatively by 8-hydroxyquinoline in the pH range 3.3-7.6. A slightly different range from pH 3.60 to 7.33 was also reported[2]. The precipitated compound was shown to be a 4-coördinated complex having the composition $MoO_2(ox)_2$. The pH range of the quantitative precipitation of the complex and its composition do not seem to be compatible with present knowledge of the pH stability of anionic and cationic molybdenum. Hence the present work was undertaken from this viewpoint.

EXPERIMENTAL

Standard solutions of sodium molybdate (16.5428 g of G.R. $Na_2MoO_4 \cdot 2H_2O$/l) and oxine (1.5617 g of G.R. $C_9H_6N \cdot OH$/250 ml) were prepared. A Marconi pH meter was used for all the pH measurements. 5 ml of sodium molybdate solution was taken and diluted to exactly 100 ml; the pH of the solution was measured and found to be 7.2. Very dilute hydrochloric acid was added so as to adjust the pH to 4.91 and then glass electrode titration was carried out using oxine solution. The results are graphically represented by curve A in Fig. 1. Similar titrations were carried out keeping the initial pH of the molybdate solution at 3.86 and 2.24 by adding the requisite amounts of acid; the results are shown by curves B and C respectively of Fig. 1. Only in the last case, where the initial pH of the molybdate solution was 2.24, was a yellow precipitate obtained; in the other two cases no precipitate was formed. This precipitate was filtered, dried and a known weight of it (0.2028 g) was taken, treated with conc. nitric acid, finally converted to molybdic oxide and weighed as MoO_3 (0.068 g).

RESULTS AND DISCUSSION

Both the reagents — molybdate and oxine — are peculiar in their behaviour. 8-Hydroxyquinoline is a weak acid[3] ($K_a = 4.2 \cdot 10^{-11}$) as well as a weak base[4] ($K_b = 1 \cdot 10^{-10}$). Several isopolymolybdates are known[5] to exist under different pH conditions. The paramolybdates are stable below pH 4.5 till the iso-electric point is reached, which is round about pH 1 where the ion changes sign and becomes a cation. Cryoscopic[6], spectrophotometric[7], and crystal structure[8] determinations of paramolybdates reveal the presence of the $Mo_7O_{24}^{-6}$ anion. The transition from one species to another is never abrupt and there will be an appreciable concentration of MoO_2^{++} ion at pH 2.24 in equilibrium with the main aggregate $Mo_7O_{24}^{-6}$ ion. Hence there are only two possible compositions for the compound obtained, *viz.*, (1) oxine paramolybdate $(ox.H)_2H_4Mo_7O_{24}$, and (2)

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molybdenyl oxinate $MoO_2(ox)_2$. These two compounds require 192.3 g and 416 g, respectively, to contain 1 gram atom of molybdenum. The results obtained correspond to 429 g, indicating definitely the latter composition. The presence of an appreciable concentration of MoO_2^{++} is a prerequisite for the formation of this insoluble complex and this explains why it is not formed at pH 3.86 and 4.91 where molybdenum is present mainly in the anionic state. Hence the curves are typical neutralisation curves (A and B in Fig. 1). When the precipitation takes place it is to be expected that the pH will fall due to the liberation of hydrogen ions according to the following equation:

$$MoO_2^{++} + 2\ H\text{-}ox \rightarrow MoO_2(ox)_2 + 2\ H^+$$

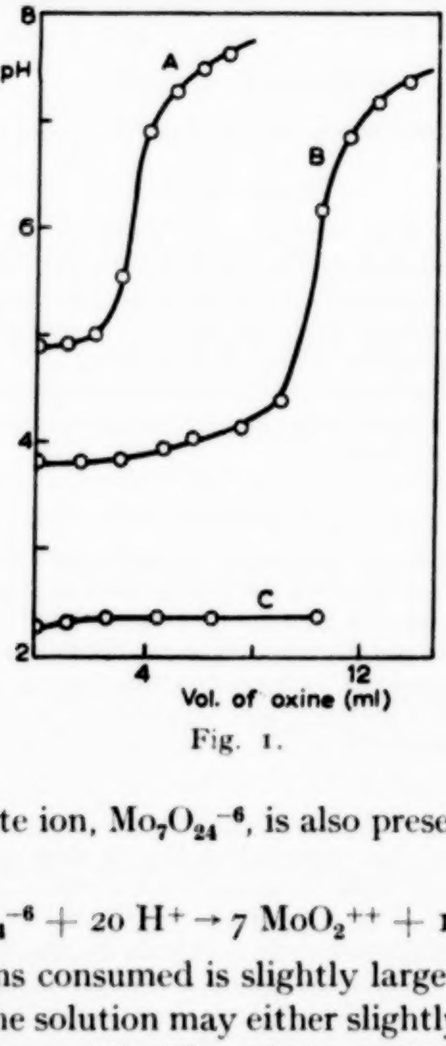

Fig. 1.

However, the paramolybdate ion, $Mo_7O_{24}^{-6}$, is also present and according to the following transformation:

$$Mo_7O_{24}^{-6} + 20\ H^+ \rightarrow 7\ MoO_2^{++} + 10\ H_2O$$

the number of hydrogen ions consumed is slightly larger than the number liberated. Hence the resultant pH of the solution may either slightly increase or remain constant for all practical purposes. Curve C in Fig. 1 is in conformity with this.

Thus it is clear that the molybdenyl oxinate cannot be formed at higher pH values and that the pH of a solution is an important controlling factor in its formation. It was reported earlier[9] that in the gravimetric estimation of uranium as oxinate, the interference of molybdate, vanadate and tungstate could be avoided by masking them using complexone at pH 8.1-8.9. This appears surprising for two reasons. Firstly, maintenance of the solution at pH 8.1-8.9 is itself sufficient to avoid the interference of molybdate. At this pH, the ion is mainly MoO_4^{-2} and the precipitation of molybdenyl oxinate is not possible. Secondly, in this pH range of 8.1-8.9, the complexone cannot mask molybdate by forming a chelate. This was shown in a recent communication[10] wherein calcium was removed in alkaline medium as $CaMoO_4$ and in the filtrate, containing excess of sodium molybdate, magnesium was chelatometrically estimated by titrating against complexone III without any error being involved.

In another communication[11] cupferron was used to precipitate titanium in the presence of MoO_4^{-2}, WO_4^{-2} and VO_4^{-3}, using the disodium salt of EDTA as a masking agent at pH between 4.3 and 7.0. This also appears surprising for the above-mentioned reasons.

Thus it becomes essential not to confuse the exact reason for achievement of selectivity, whether it is due to masking the other elements by chelation or by simple control of the pH of the solution. It becomes all the more important when molybdenum is concerned, since the several polyanionic species and the cation have different pH ranges of stability.

The conditions for the formation of a stable molybdenum chelate with complexone are under investigation.

ACKNOWLEDGEMENT

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SUMMARY

Molybdenum was reported to be precipitated quantitatively by 8-hydroxyquinoline in the pH range 3.3-7.6, the precipitated compound having the composition $MoO_2(ox)_2$. The pH range reported and the composition of the complex do not seem to be compatible with present knowledge of the pH stability of anionic and cationic molybdenum. It is now shown that under defined conditions, the precipitate is not formed at pH values higher than 2.24. In several estimations of other metals, molybdenum was masked by using a complexone at high pH values. It is now pointed out, that maintaining the solution at high pH value is itself sufficient and no other external complexing agent is necessary for masking molybdenum.

RÉSUMÉ

Il a été rapporté que le molybdène est précipité quantitativement par le 8-hydroxy-quinoléine aux pH de l'ordre de 3.3 à 7.6 et que le composé précipité a la composition suivante: $MoO_2(ox)_2$. Les pH envisagés et la composition du complexe ne paraissent pas compatibles avec la connaissance actuelle de la stabilité de pH du molybdène anionique et cationique. On montre que dans des conditions définies, le précipité ne se forme pas à un pH supérieur à 2.24. Dans plusieurs dosages d'autres métaux, on a masqué le molybdène en utilisant un complexon à pH élevé. On a maintenant noté qu'il est suffisant pour cela de maintenir élevé le pH de la solution, sans utiliser un agent complexant extérieur.

ZUSAMMENFASSUNG

Es ist früher mitgeteilt worden, dass das Molybdän in dem pH-Bereich 3.3-7.6 quantitativ durch 8-Oxychinolin gefällt wird und dass die Zusammensetzung des entstandenen Niederschlages der Formel $MoO_2(ox)_2$ entspricht. Der mitgeteilte pH-Bereich und die Zusammensetzung der Verbindung scheinen aber mit dem gegenwartigen Stande der Kenntnis über die pH-Beständigkeit des anionischen und kationischen Molybdäns nicht vereinbar zu sein. Es wurde nun gezeigt, dass unter bestimmten Bedingungen, der Niederschlag sich bei höheren pH-Werten als 2.24 nicht bildet. Bei verschiedenen Bestimmungen anderer Metalle ist das Molybdän mit Hilfe eines Komplexons bei hohen pH-Werten getarnt worden. Es wurde nun gezeigt, dass es, um das Molybdän zu tarnen, genügt den pH-Wert der Lösung hoch zu halten ohne ein komplexierendes Agens zuzufügen.

REFERENCES

[1] H. GOTO, *J. Chem. Soc. Japan.*, 54 (1933) 725; 56 (1935) 314.
[2] H. R. FLECK AND A. M. WARD, *Analyst*, 58 (1933) 388; 62 (1937) 378.
[3] K. G. STONE AND L. FRIEDMAN, *J. Am. Chem. Soc.*, 69 (1947) 209.
[4] R. BERG. *Das o-Oxychinolin*, Vol. 34, 2nd ed., Enke, Stuttgart, 1938.
[5] G. JANDER *et al.*, *Z. anorg. Chem.*, 194 (1930) 383; 215 (1933) 310.
[6] J. BYE, *Ann. chim.*, 20 (1945) 463.
[7] I. LINDQVIST, *Acta Chem. Scand.*, 5 (1951) 568.
[8] J. H. EVANS, *J. Am. Chem. Soc.*, 70 (1948) 129.
I. LINDQVIST, *Arkiv Kemi*, 2 (1950) 325.
[9] R. S. SENSARMA AND A. K. MALLIK, *Anal. Chim. Acta*, 12 (1955) 329.
[10] D. V. RAMANA RAO, *Current Sci. (India)*, communicated.
[11] A. K. MAJUMDAR AND J. B. RAYCHOWDHURY, *Anal. Chim. Acta*, 15 (1956) 105.

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ELECTRO-CHROMATOGRAPHY IN THE SEPARATION OF IONS

PART III. SEPARATION OF SILVER GROUP METALS

by

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In a previous publication MAJUMDAR AND MUKHERJEE[1] recorded the migration sequences of some of the sulphide group members in a number of common reagents, which acted both as electrolytes and as complexing reagents. Separation of several binary, ternary and quaternary mixtures of the sulphide group members was shown to be possible by the application of a potential of 150 V for 5 hours with electrolyte concentration of 0.1*N*. Recently MAJUMDAR AND CHAKRABARTTY[2], during their work on the separation of precious metals in microgram quantities, observed that the platinum metals including gold, even when present in a quaternary mixture, could be easily separated from each other.

The present study is a continuation of the work undertaken to separate by electrochromatography the mixtures of inorganic ions usually met with in minerals or in qualitative group separation schemes. This paper records the movements and the migration sequences of Ag^+, Hg_2^{+2}, Pb^{+2} and Tl^+ in different complex-forming electrolytes, and it has been found that out of about thirty such electrolytes only sodium chloride, potassium chloride and potassium cyanide are effective for the complete separation of all the four ions from a quaternary mixture, when subjected to a potential of 150 V over a period of 3 hours.

EXPERIMENTAL

The apparatus and technique used were exactly similar to those reported in earlier papers[1,2]. Filter paper strips from Whatman filter paper No. 2, size 44 cm × 1 cm, were used and a mixture of solutions of the nitrates of the ions was put on the strip in the form of a small drop (0.01 ml) containing about 15 μg of each ion. A potential of about 150 V was maintained for a period of 3 h. The electrolytes used were of the same strength, usually 0.1*N*.

Out of about thirty electrolytes, HNO_3, HCl, H_2SO_4, H_3PO_4, $HClO_4$, acetic acid, oxalic acid, tartaric acid, citric acid, malonic acid, Na citrate, Na K tartrate, Na_2CO_3, NaOH, NH_4OH, $CH_3CO_2NH_4$, NH_4Cl, NH_4CNS, NH_4NO_3, CH_3CO_2Na, NaCl, $NaNO_2$, NaBr, $Na_2S_2O_3$, KI, KCl, KCN (aqueous, and in solution acidified with acetic acid to pH 7.0), EDTA (aqueous, in 0.1*N* ammonia solution and in acetate buffer at pH 4.8) and thiourea (aqueous, in acetate buffer at pH 5.8 and in 0.1*N* HCl solution), nearly a dozen responded in a manner such that the difference in ionic migration of the elements made possible the separation of a ternary or a quaternary mixture. Under the conditions of the experiment, the degree of reproducibility was highly satisfactory.

The results of the ionic migration are given in Table I, and Table II shows the migration sequences of the elements present in ternary or quaternary mixtures.

TABLE I

EFFECT OF ELECTROLYTES (0.1*N*) ON IONIC MOVEMENTS IN cm

Ions	*HNO_3*	*HCl*	*H_2SO_4*	*H_3PO_4*	*$HClO_4$*	*CH_3CO_2H*	*Oxalic acid*	*Tartaric acid*	*Citric acid*	*Malonic acid*	*Na citrate*	*Na K tartrate*
Pb^{+2}	—2.8	—2.7	0.0	0.0	—6.3	—2.3	0.0	—3.4	—2.9	—7.4	+3.2	+0.6
Ag^+	(+0.2 to —1.5)	0.0	(+0.3 to —1.4)	(+0.4 to —3.0)	(+0.3 to —1.6)	0.0	0.0	0.0	(+0.3 to —1.4)	(+0.5 to —1.5)	0.0	0.0
Hg_2^{+2}	—0.9	+4.9	0.0	—0.9	—1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Tl^+	—5.2	—3.0	—6.7	—10.7	—8.6	—11.7	—12.5	—10.2	—17.2	—13.0	—2.3	—6.3

Ions	*Na_2CO_3*	*NaOH*	*NH_4OH*	*$CH_3CO_2NH_4$*	*NH_4Cl*	*NH_4CNS*	*NH_4NO_3*	*CH_3CO_2Na*	*NaCl*	*$NaNO_2$*	*NaBr*	*$Na_2S_2O_3$*
Pb^{+2}	0.0	0.0	0.0	—1.1	—2.5	—1.9	—1.8	(+0.5 to —1.5)	—2.2	—0.5	—0.5	+4.7
Ag^+	0.0	0.0	0.0	(+0.3 to —1.5)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0
Hg_2^{+2}	0.0	0.0	0.0	(+0.3 to —3.0)	+5.2	0.0; +6.1	0.0	0.0	0.0; +4.8	+1.1	0.0; +4.8	0.0; +6.4
Tl^+	—6.0	—5.1	—11.0	—11.1	—8.6	—8.0	—10.4	—10.7	—6.4	—9.9	0.0	+1.4

Ions	*KI*	*KCl*	*KCN (aq.)*	*KCN (pH 7.0)*	*EDTA (aq.)*	*EDTA (0.1N NH_4OH)*	*EDTA (pH 4.8)*	*Thiourea (aq.)*	*Thiourea (pH 5.8)*	*Thiourea (0.1N HCl)*
Pb^{+2}	0.0	—2.5	0.0	0.0	+5.1	+1.5	+3.6	0.0	—1.0	—2.7
Ag^+	0.0	0.0	+4.5	+5.9	0.0	0.0	0.0	—0.4	0.0; —2.6	—2.0
Hg_2^{+2}	0.0; +6.5	0.0; +4.5	0.0; +7.0	+2.6	+4.6	+2.4	+3.2	0.0; —1.7	0.0; —3.8	—1.6
Tl^+	0.0	—7.0	—5.5	—7.4	—6.1	+3.7	—6.7	—6.3	—7.9	—7.7

TABLE II

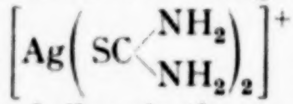
MIGRATION SEQUENCES OF IONS PRESENT IN TERNARY OR QUATERNARY MIXTURES

Electrolytes (0.1N)	*Sequence of separation*
HNO_3, $HClO_4$, CH_3CO_2H, tartaric acid, citric acid, malonic acid	: Ag, Pb, Tl—
NH_4NO_3	: [Ag, Pb], Tl—
$Na_2S_2O_3$	+ Ag, Pb, Tl:; + Hg, Pb, Tl:
HNO_3, NH_4NO_3, $HClO_4$, CH_3CO_2H, tartaric acid, citric acid, malonic acid	: Hg, Pb, Tl—
EDTA (aq. and pH 4.8), Na citrate, Na K tartrate	+ Pb: Ag, Tl—
EDTA (aq. and pH 4.8), HCl, NH_4Cl, NH_4CNS	+ Hg: Ag, Tl—
NH_4Cl, NH_4CNS	+ Hg: Pb, Tl—
HCl	+ Hg: Ag, Pb—
Na citrate, Na K tartrate	+ Pb: Hg, Tl—
Thiourea (pH 5.8)	:Pb, Hg, Tl—; :Ag, Hg, Tl—
EDTA (0.1*N* ammonia)	+ Tl, Hg, Ag:; + Tl, Pb, Ag:
HCl	+ Hg: Ag, [Pb, Tl] —
NH_4Cl, NH_4CNS	+ Hg: [Ag, Pb], Tl—
NaCl, KCl	+ Hg: Ag, Pb, Tl—
KCN (aq.)	+ Hg, Ag: Pb, Tl—
KCN (pH 7.0)	+ Ag, Hg: Pb, Tl—

DISCUSSION

The ionic movements are obtained by measuring the distance from the centre of the original spot to the centre of the electrochromatogram. The + sign signifies the movement of the ion towards the anode while the — sign corresponds to movement towards the cathode, the symbol : is the starting point. Sometimes diffusion and expansion of the zone size are associated with the ionic movements and the amount of spreading or elongation due to such effects is given in parentheses (*cf.* Table I). The ions enclosed in square brackets have a slight common migration zone.

Lead ion behaves mostly as a cation except in electrolytes such as Na citrate, Na K tartrate, thiosulphate and EDTA, where it forms anionic complexes.

Silver as cation shows no appreciable movement except perhaps by diffusion when it forms a comet-like band due to a large tailing. Only in the presence of thiourea does the cationic complex  $\left[\mathrm{Ag}\left(\mathrm{SC}\begin{matrix}\diagup \mathrm{NH_2}\\ \diagdown \mathrm{NH_2}\end{matrix}\right)_2\right]^+$ leave the centre and form a well-defined band. The movement of silver in the presence of decinormal ammonia is zero, as only silver oxide is formed at the centre and the concentration of ammonia is not enough to form the complex; if the strength of ammonia is increased (0.5*N* to 5*N*), the cationic silver complex shows a movement of nearly —10 cm. As an anionic complex in the presence of potassium cyanide (aq. and at pH 7.0) and thiosulphate its movement is considerable.

Mercurous ion is cationic only in nitric, phosphoric and perchloric acids and thiourea, while it is anionic with other electrolytes. With solutions of sodium chloride, sodium bromide, potassium chloride, potassium iodide, potassium cyanide, ammonium thiocyanate, sodium thiosulphate and thiourea (aq. and at pH 5.8), mercurous ion leaves a small black streak at the centre of the original spot, which may be due to mercury from the decomposition of a fraction of the Hg_2^{+2} ion to Hg and Hg^{+2}.

Thallous ion usually shows an appreciable movement which may be due to its low adsorption by the paper and high resistance to complex formation. Only with thiosulphate and ammoniacal EDTA does it form an anionic complex.

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The possible separations with the sequence can be well predicted from the table of ionic movements. In a few instances, *e.g.* with HCl, NH_4NO_3, NH_4Cl, NH_4CNS, owing to the slight overlapping of the zones, the expected results are, however, not attained. Ionic movements and migration sequences depend on the change in pH of the electrolytes, which determines the formation and stability of a complex. In aqueous potassium cyanide solution, the sequence of the four ions is Hg - Ag - Pb - Tl but when the cyanide solution is acidified with acetic acid the sequence changes to Ag - Hg - Pb - Tl.

SUMMARY

The migration sequences of silver group ions Ag^+, Hg_2^{+2}, Pb^{+2} and Tl^+ have been studied in a number of complex-forming electrolytes. Based on the migration sequences, the ions in a mixture can be separated into distinct zones using a decinormal solution of sodium chloride, potassium chloride or potassium cyanide as the electrolyte. The sequence is Hg - Ag - Pb - Tl, while in KCN at pH 7.0 the sequence becomes Ag - Hg - Pb - Tl.

RÉSUMÉ

Les séquences de migration des ions du groupe de l'argent, Ag^+, Hg_2^{+2}, Pb^{+2} et Tl^+ ont été étudiées dans plusieurs électrolytes formant des complexes. En se basant sur ces séquences de migration, les ions d'un mélange ont été séparés en zones distinctes, en utilisant une solution décinormale de chlorure de sodium, de chlorure de potassium ou de cyanure de potassium comme électrolyte. L'ordre est Hg - Ag - Pb - Tl, tandis que dans la solution de cyanure de potassium, à pH 7.0, l'ordre devient Ag - Hg - Pb - Tl.

ZUSAMMENFASSUNG

Die Wanderungsreihenfolge der Ionen der Silbergruppe Ag^+, Hg_2^{+2}, Pb^{+2} und Tl^+ wurde in einer Anzahl von komplexbildenden Elektrolyten untersucht. Auf Grund der Wanderungsreihenfolge können die Ionen eines Gemisches mit einer dezinormalen Lösung von Natriumchlorid, Kaliumchlorid oder Kaliumcyanid als Elektrolyt in deutliche Zonen geschieden werden. Die Reihenfolge ist Hg - Ag - Pb - Tl, in KCN bei pH 7.0 Ag - Hg - Pb - Tl.

REFERENCES

[1] A. K. Majumdar and H. G. Mukherjee, *Anal. Chim. Acta*, 15 (1956) 547.
[2] A. K. Majumdar and M. M. Chakrabartty, *Anal. Chim. Acta*, 17 (1957) 228.

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INTERFERENCES OF THREE ELEMENTS IN FLAME PHOTOMETRY

Cr-Co-Mn SYSTEM*

by

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INTRODUCTION

In some of our papers[1,2,3] we have made some references to the interference systems that are called *interference triple systems* in flame photometry. These triple systems must be taken into consideration whenever three elements or compounds are present in the solution being analysed, especially when the compounds contain elements that can be excited in the source.

Sometimes one of the components — when it is excitable — causes radiation interference if it modifies the excitation conditions of the other components of the solution, thus producing an enhancement or depression of the intensity of their emissions[4,5,6].

In our laboratories several triple systems have been studied, but in this paper the details of only one of these systems are given. This system, which has recently been exhaustively studied by one of the authors[7], consists of: *chromium*, *cobalt* and *manganese*. The mutual interferences of these elements have been examined in nearly neutral aqueous and acid solutions.

The systems of two elements (double systems), such as Cr/Co, Co/Cr, Cr/Mn, Mn/Cr, Co/Mn and Mn/Co, that belong to the triple system considered here, have already been described in other papers[1,2,8]. To solve the problem of the interferences in the system formed by these three elements, we have used the procedure proposed by two of the authors[9], in which the *ponderal interference ratios* are used. By this method the *interference ratios* are corrected according to the concentration of each of the components present in the solution (analysis elements or components which, even when not being analysed, have interferential effects on the element being determined in the flame photometer).

PONDERAL RATIOS

The ponderal ratios we use are given by the following equation:

$$R_p = \frac{[\text{I.E.}]}{[\text{A.E.}]}\left([\text{I.E.}] + [\text{A.E.}]\right) \quad \ldots\ldots\ldots\ldots \quad (1)$$

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where I.E. = interfering element and A.E. = analysis element. Here [I.E.] and [A.E.] are the concentrations found experimentally in the flame photometer for the interfering element and the analysis element in each system of two elements. The ponderal ratio should in fact be given as a function of the values $[\text{I.E.}_\text{E}]$ and $[\text{A.E.}_\text{E}]$, the experimental values, which are different from the values $[\text{I.E.}_\text{T}]$ and $[\text{A.E.}_\text{T}]$, the added concentrations or theoretical values of the concentration.

As indicated in further sections of this paper, in practice, the logarithms ($\log R_p$) of these ponderal ratios are used instead of the actual ratios.

In order to study systems of three elements the ponderal ratio of each element, as analysis element, has to be considered, the other two acting in each case as interfering element.

Systems of two elements

In systems of two elements these ponderal ratios have been used to obtain linear equations as follows:

$$F_c = m \log R_p + b \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

in which a conversion factor F_c has been introduced, whose value is given by

$$F_c = \frac{[\text{A.E.}_\text{T}]}{[\text{A.E.}_\text{E}]}$$

The factor F_c is at the same time (see equation (2)) a function of the ponderal ratio R_p. When this function is represented graphically several different straight lines are obtained, one for each value of the concentration $[\text{A.E.}_\text{T}]$*.

On the graphs these straight lines represent the variation of the conversion factor F_c as a function of the ponderal ratio. The straight lines obtained by this method represent not only the variations of the ratio of the concentrations of the analysis element — added and experimental values — as conversion factor, but they also provide a means of correcting the experimental results, if the shape and situation of these lines on the graph paper is known beforehand. They may be used to obtain the factors F_c graphically, starting from the concentration values obtained experimentally from the readings taken in the flame photometer**.

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* It must be remembered that even when using experimental values to plot the lines given by equation (2) the experimental points are found on straight lines, each one consisting of a group of points which belong to solutions containing the same amount of analysis element. For each of these solutions the condition $[\text{A.E.}_\text{T}]$ = constant, is valid.

** From the details given here it may be deduced that a preliminary study must be made of the behaviour of solutions prepared with known concentrations of analysis and interfering elements. These solutions are used to plot the straight lines. Afterwards, when the analysis of an unknown solution is made, the ponderal ratios R_p are calculated using the experimental values and, by means of the corresponding logarithms, the conversion factors F_c can be found on the graphs. Multiplication of the experimental values by the factors gives the corrected values of the concentration[9].

Systems of three elements

The application of the ponderal ratios used in the systems of two elements, may be extended to systems of three elements if the behaviour of the several double systems of which they consist are already known.

Average ponderal ratios, R_{pm}, may be obtained according to the following equation:

$$\log R_{pm} = \tfrac{1}{2} (\log R_p/F_c) + \tfrac{1}{2} (\log R_p'/F_c') \quad \ldots\ldots\ldots\ldots \quad (3)$$

derived from two interference ratios, also ponderal, which have been calculated for each interfering element with the element considered as analysis element. The ratio R_{pm} is thus corrected in particular and proportionally by means of the binary conversion factors F_c and F_c'.

For this average ponderal ratio the following relation also holds:

$$F_{cm} = m_1 \log R_{pm} + b_1$$

Here F_{cm} has the value

$$F_{cm} = \frac{[\text{A.E.}_\text{T}]}{[\text{A.E.}_\text{E}]}$$

in which $[\text{A.E.}_\text{E}]$ is the concentration of the analysis element experimentally obtained, using a solution in which the other two elements are also present.

EXPERIMENTAL PART

Apparatus and experimental conditions

Apparatus

Beckman Flame Spectrophotometer model DU No. 9200. Phototubes: non-multiplier.

Gases. Acetylene and oxygen.

Pressures. 10 pounds per square inch for oxygen, being adjusted on the basis of the optimum for acetylene (5 pounds per square inch). The oxygen pressure depends on the make of the burner.

Pressure regulation. Double regulators with diaphragm and needle valves at the outlets of the gas containers. Beckman regulator between these and the atomising burner.

Experimental conditions

Slit. The slit width was adjusted according to the sensitivity of the analysis elements. Rather wide slits were used: Cr 425.4 mμ = 0.4 mm; Co 353.0 mμ = 0.7 mm and Mn 403.3 mμ = 0.3 mm.

Instrumental sensitivity. Sensitivity selector in position 0.1; sensitivity control at maximum; 10,000 megohm resistance.

Wave length selection. See wave lengths metioned above.

Phototube. "Blue" phototube for all the elements.

Solutions

Stock solutions

The standard solutions — dilution series — and the solutions used for the preliminary study of interferences were prepared from stock solutions containing the analysis elements in concentrations ten times higher than the concentration of the highest standard solution.

Standard solutions

The standard solutions mentioned here and the "blanks" were used to plot the calibration curves.

Dilution series. The limits of the concentration range used for each element were 0 to 4000 p.p.m. for Cr and 0 to 1000 p.p.m. for Co and Mn. From the highest concentration of these ranges successive dilutions were prepared, using the following dilution factors: 1/2, 1/5 and 1/10.

Background solutions. Since two series of solutions were prepared (aqueous and acid), the dilutions of the standards were made by means of two background solutions: (a) distilled water and (b) acid solution containing 6 ml of conc. H_2SO_4 per 100 ml.

Blanks. The background solutions have been used as blanks.

Solutions prepared for the study of the systems of two elements

In order to study the interference systems of two elements, solutions containing 50, 200 and 500 p.p.m. of Co or Mn and 200, 800 and 2000 p.p.m. of Cr were prepared. Nine solutions for each couple of elements.

Solutions prepared for the study of the systems of three elements

The same concentrations mentioned above were used to prepare 27 triple solutions. All the acid solutions that were prepared according to the details given above contained 30 p.p.m. of Fe and 6 ml of conc. H_2SO_4 per 100 ml. This iron concentration corresponds to the concentration of this element remaining in the test solution after the iron has been extracted, before beginning the analysis of the other elements of the ferrous alloys[2].

Graphs

From the calculated conversion factors and ponderal ratios, the lines F_c *versus* log R_p and F_{cm} *versus* log R_{pm}, were plotted graphically. From these graphs we have calculated also graphically the corresponding equations of each one of the straight lines which represent the variations of the conversion factors as a function of the ponderal ratios.

TABLE I

LINEAR FUNCTIONS USED FOR CORRECTION OF RESULTS

Interferences of two elements

Systems	*A.E.*	*A.E. concentration (p.p.m.)*	*Functions*	
			Aqueous solutions	*Acid solutions*
Co/Cr	Cr	2000	$F = -0.115 \log R_p + 1.37$	$F = 0.65 \log R_p - 0.75$
		800	$F = -0.305 \log R_p + 1.86$	$F = -0.082 \log R_p + 1.28$
		200	$F = -0.295 \log R_p + 1.61$	$F = -0.715 \log R_p + 3.12$
Mn/Cr	Cr	2000	$F = -0.14 \log R_p + 1.36$	$F = -0.042 \log R_p + 1.25$
		800	$F = -0.24 \log R_p + 1.55$	$F = -0.172 \log R_p + 1.54$
		200	$F = -0.093 \log R_p + 0.98$	$F = -0.89 \log R_p + 3.70$
Cr/Co	Co	500	$F = -0.15 \log R_p + 1.26$	$F = -0.207 \log R_p + 1.36$
		200	$F = -0.363 \log R_p + 1.98$	$F = -0.18 \log R_p + 1.05$
		50	$F = -0.326 \log R_p + 1.48$	$F = -0.105 \log R_p + 0.53$
Mn/Co	Co	500	$F = -0.13 \log R_p + 1.07$	$F = -0.147 \log R_p + 1.25$
		200	$F = -0.325 \log R_p + 1.66$	$F = -0.23 \log R_p + 1.33$
		50	$F = -0.655 \log R_p + 2.40$	$F = -0.182 \log R_p + 0.94$
Cr/Mn	Mn	500	$F = 0.15 \log R_p + 0.77$	$F = 0.017 \log R_p + 0.87$
		200	$F = 0.055 \log R_p + 1.00$	$F = -0.025 \log R_p + 0.98$
		50	$F = -0.155 \log R_p + 1.59$	$F = -0.097 \log R_p + 0.96$
Co/Mn	Mn	500	$F = 0.185 \log R_p + 0.52$	$F = -0.062 \log R_p + 1.18$
		200	$F = 0.235 \log R_p + 0.47$	$F = -0.01 \log R_p + 1.03$
		50	$F = 0.048 \log R_p + 0.93$	$F = 0.052 \log R_p + 0.70$

Equations of the straight lines

Systems F_c *versus* $\log R_p$ *(systems of two elements)*. See Table I.
Systems F_{cm} *versus* $\log R_{pm}$ *(systems of three elements)*. See Table II.

Conversion of the straight lines for extreme concentrations into the straight line corresponding to intermediate concentration

We have also calculated the equations to convert the values $\log R_p$ corresponding to the extreme values of the concentration of the analysis element (higher and lower concentrations) into values X which belong to the central straight line — intermediate concentration of the analysis element. In the systems of three elements the equations that transform $\log R_{pm}$ into X_m have also been calculated. See some examples in Table III.

TABLE II

LINEAR FUNCTIONS USED FOR CORRECTION OF RESULTS

Interferences of three elements

Systems	*A.E.*	*A.E. concentration (p.p.m.)*	*Functions*	
			Aqueous solutions	*Acid solutions*
		2000	$F = -0.03 \log R_p + 1.00$	$F = -0.125 \log R_p + 1.36$
Co, Mn/Cr	Cr	800	$F = -0.075 \log R_p + 1.05$	$F = -0.142 \log R_p + 1.43$
		200	$F = -0.255 \log R_p + 1.46$	$F = -0.17 \log R_p + 1.28$
		500	$F = -0.21 \log R_p + 1.85$	$F = -0.132 \log R_p + 1.64$
Cr, Mn/Co	Co	200	$F = -0.095 \log R_p + 1.02$	$F = -0.097 \log R_p + 1.12$
		50	$F = -0.05 \log R_p + 1.05$	$F = -0.035 \log R_p + 0.77$
		500	$F = 0.505 \log R_p$	$F = 0.052 \log R_p + 0.76$
Cr, Co/Mn	Mn	200	$F = 0.15 \log R_p + 0.85$	$F = -0.042 \log R_p + 1.06$
		50	$F = -0.19 \log R_p + 1.70$	$F = -0.105 \log R_p + 1.22$

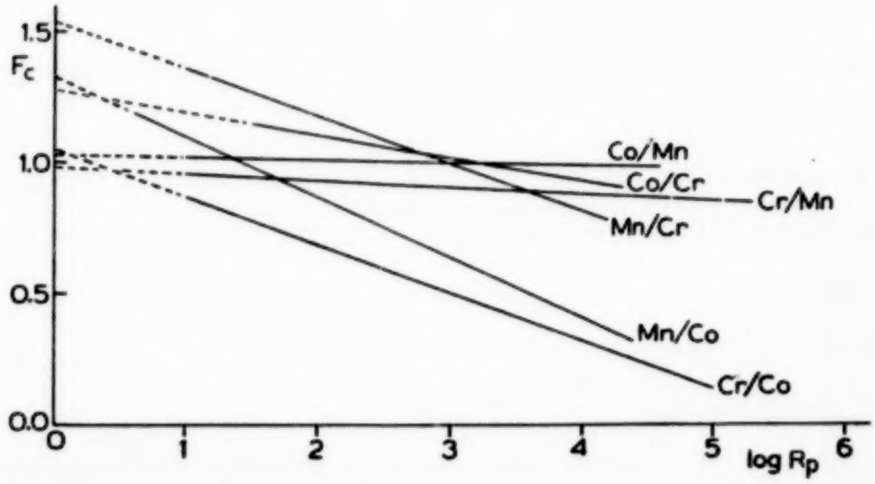

Fig. 1. Correction straight lines for acid systems. Interference systems of two elements.

Shape of the graphs

The above-mentioned table and others that we have used for the other analysis elements have been derived from graphs represented in the figures mentioned in the following sections.

References p. 558

TABLE III

LINEAR FUNCTIONS USED FOR THE CONVERSION OF R_p VALUES*

Interferences of two and three elements with chromium

Systems	*A.E.*	*A.E. concentration (p.p.m.)*	*Functions*	*log p.p.m. A.E.*	*m*	*b*
Interferences of two elements						
Aqueous solutions						
		From 2000 into 800	$X = 0.377 \log R_p + 1.61$	3.30	0.377	1.61
Co/Cr	Cr	800		2.90	1.00	0.0
		From 200 into 800	$X = 0.967 \log R_p + 0.82$	2.30	0.967	0.82
		From 2000 into 800	$X = 0.583 \log R_p + 0.79$	3.30	0.583	0.79
Mn/Cr	Cr	800		2.90	1.00	0.0
		From 200 into 800	$X = 0.388 \log R_p + 2.38$	2.30	0.388	2.38
Acid solutions						
		From 2000 into 800	$X = -7.93 \log R_p + 24.75$	3.30	−7.93	24.75
Co/Cr	Cr	800		2.90	1.00	0.0
		From 200 into 800	$X = 8.72 \log R_p - 22.4$	2.30	8.72	−22.4
		From 2000 into 800	$X = 0.244 \log R_p + 1.68$	3.30	0.244	1.68
Mn/Cr	Cr	800		2.90	1.00	0.0
		From 200 into 800	$X = 5.18 \log R_p - 12.55$	2.30	5.18	−12.55

Systems	*A.E.*	*A.E. concentration (p.p.m.)*	*Functions*	*log p.p.m. A.E.*	m_1	b_1
Interferences of three elements						
Aqueous solutions						
		From 2000 into 800	$X_m = 0.40 \log R_{pm} + 0.67$	3.30	0.40	0.67
Co, Mn/Cr	Cr	800		2.90	1.00	0.0
		From 200 into 800	$X_m = 3.40 \log R_{pm} - 5.47$	2.30	3.40	−5.47
Acid solutions						
		From 2000 into 800	$X_m = 0.88 \log R_{pm} + 0.50$	3.30	0.88	0.50
Co, Mn/Cr	Cr	800		2.90	1.00	0.0
		From 200 into 800	$X_m = 1.20 \log R_{pm} + 1.06$	2.30	1.20	1.06

* Tables similar to this have been used for cobalt and manganese in the case of interferences of two and three elements in acid and aqueous solutions.

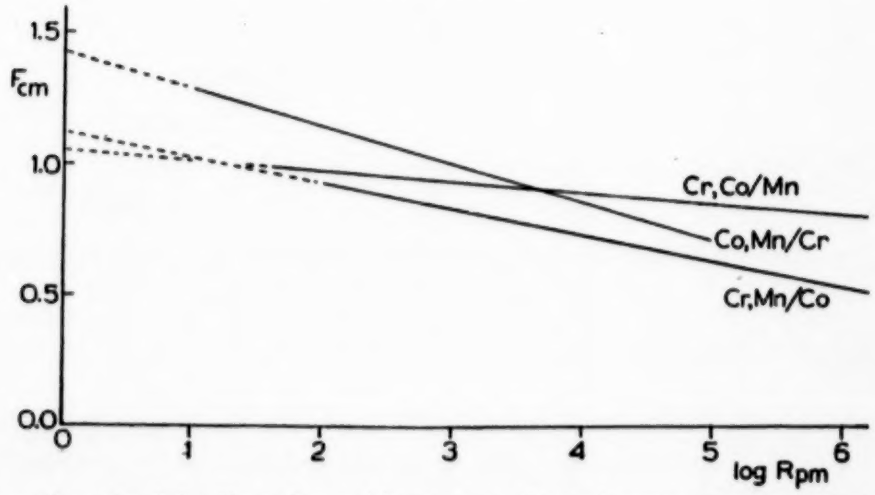

Fig. 2. Correction straight lines for acid systems. Interference systems of three elements.

Correction curves. In Figs. 1 and 2 we have only given the straight lines used for the correction of experimental results. They correspond to the intermediate concentration of the analysis element.

Auxiliary curves. The values m, b, m_1 and b_1 taken from Table III and similar tables, have been used to plot the graphs which represent the variation of these values as a function of the concentration of the analysis element. These graphs are used as auxiliary curves in the correction method described later. In Figs. 3 and 4 these graphs are given for various systems. Similar curves have been obtained for aqueous systems.

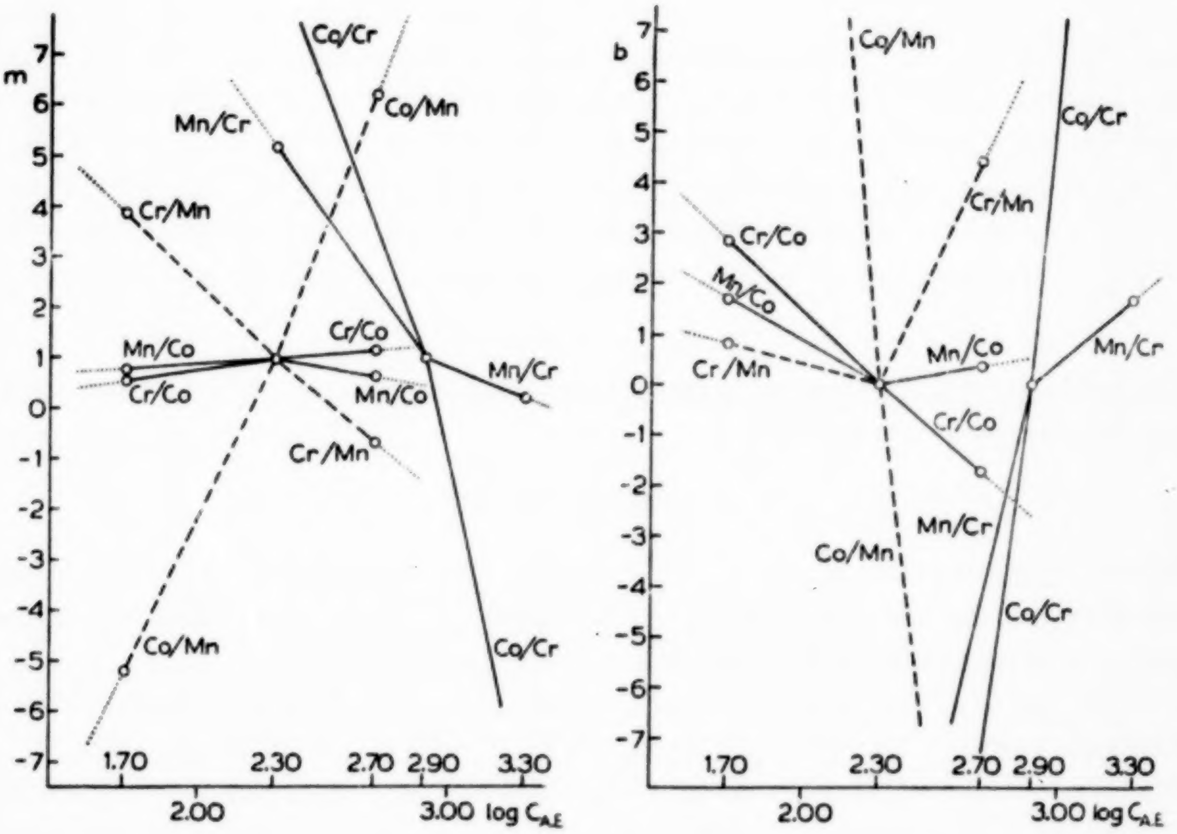

Fig. 3. Auxiliary curves for acid systems. Interference systems of two elements.

Correction methods

In this section a summary is given of the correction methods proposed by two of the authors[9].

Systems of two elements

Method for the correction of experimental values by means of single correction straight lines. In the flame photometer two experimental values [A.E.$_{\mathrm{E}}$] and [I.E.$_{\mathrm{E}}$] can be obtained. To correct these values, each element is considered as analysis element in turn, if the correction of both of them is desired. If not, the correction is carried out on only one of them. The following operations are effected:

(a) Calculation of the value R_p and of its logarithm for each solution, using the experimental values.

(b) Determination of the corresponding values m and b from the curves m *versus* log [A.E.] and b *versus* log [A.E.].

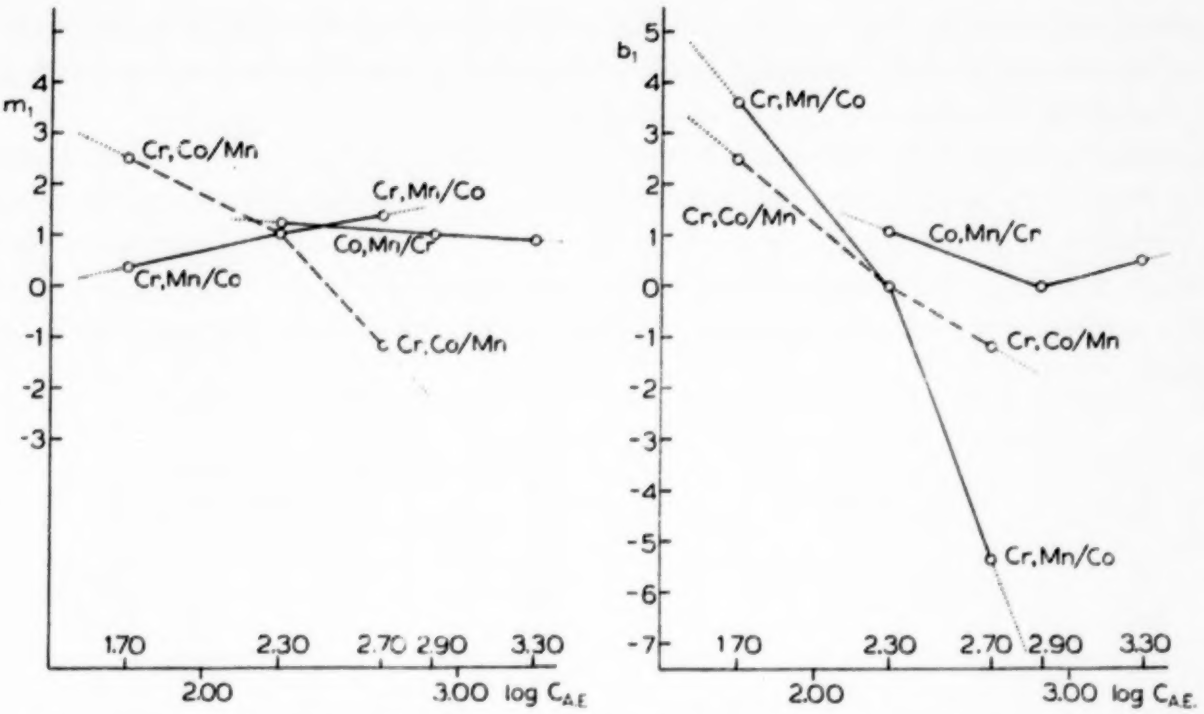

Fig. 4. Auxiliary curves for acid systems. Interference systems of three elements.

(c) Calculation of the corrected ponderal ratios X by means of the values m, b and log R_p, using the equation

$$X = m \log R_p + b.$$

(d) Determination of the factor F_c on the correction straight line. This factor may be calculated from the equation of the straight line if the curve does not cover the value X that has been calculated according to (c).

Use of the factor F_c. The product of F_c and $[\text{A.E.}_\text{E}]$ is then calculated. This gives a calculated value of the concentration, $[\text{A.E.}_\text{C}]$, which is very near to $[\text{A.E.}_\text{T}]$. The difference $[\text{A.E.}_\text{C}] - [\text{A.E.}_\text{T}]$ gives an idea of the deviations of the correction method.

Systems of three elements

Method for the correction of experimental values by means of single correction straight lines. In the analysis of three elements, Me′, Me″ and Me‴, with the flame photometer, three experimental values are obtained: $[\text{Me}'_\text{E}]$, $[\text{Me}''_\text{E}]$ and $[\text{Me}'''_\text{E}]$, each of which may be considered as belonging to an analysis element, the other two then referring to interfering elements in the triple system. If all of them are to be considered as analysis elements, the following operations have to be carried out:

(a) The values log R_p are calculated for each pair of elements. This is done for six systems as if they were double interference systems.

(b) The factors F_c are then calculated and also the values log R_{pm} for each element. See the complete procedure in the section dealing with systems of two elements.

(c) The factors F_{cm} are finally calculated. The conversion of the values log R_{pm} into X_m is similar to that described for systems of two elements.

Use of the factor F_{cm}. The product of the factor F_{cm} and the experimental values mentioned above, gives calculated values very near to the actual values of the concentration of the elements in the solution being analysed.

Double correction

Since the values m, b, m_1 and b_1 have to be calculated from auxiliary curves obtained from values [A.E.$_E$], which are the only experimental results, these values are sometimes quite different from actual concentrations. The values of the constants found on the graphs may therefore be erroneous. In such a case a double correction must be performed.

Systems of two elements. A calculated value of the concentration of the analysis element is determined. Using this intermediate value the corresponding constants are calculated on the auxiliary graphs and a second conversion factor F_c is determined. This new conversion factor is used with the original experimental value of the concentration found in the flame photometer.

Systems of three elements. Each analysis element is corrected with respect to each interfering element, since we are dealing with double interference systems. From the two calculated values of the concentration an average value is then determined. With this average value the values m_1 and b_1 are calculated on the auxiliary curve, the latter values afterwards being used in the general procedure[7].

Correction of results

We include here some tables showing results obtained by means of the correction methods described in this paper.

TABLE IV

CORRECTION OF RESULTS

Interferences of two elements (aqueous solutions)

		Added p.p.m.		*Found p.p.m.*		*Corrected p.p.m.*		*Differences p.p.m.*		
System	*A.E.*	*I.E.*	*A.E.*	*I.E.*	*A.E.*	*(I)*	*(II)*	*(U)*	*(I)*	*(II)*
Co/Cr	Cr	200	2000	389	1896	2009	2009	—104	9	9
		200	800	272	724	767	767	76	33	33
		200	200	198	232	204	199	32	4	—1
Mn/Cr	Cr	50	2000	60	1891	2305	1999	199	305	—1
		500	800	379	868	800	772	68	0	28
		500	200	425	329	243	233	129	43	33
Cr/Co	Co	2000	500	1944	731	554	511	231	54	11
		800	200	724	272	190	200	72	—10	0
		200	50	200	86	61	53	36	11	3
Mn/Co	Co	50	500	44	600	474	522	100	—26	22
		200	200	189	234	196	199	34	—4	1
		500	50	507	173	97	72	123	47	22
Cr/Mn	Mn	2000	500	2020	362	510	503	—138	10	3
		2000	200	1896	163	192	198	—37	—8	—2
		800	50	688	51	63	52	1	13	2
Co/Mn	Mn	50	500	173	507	487	487	7	—13	—13
		200	200	234	189	207	207	—11	7	7
		200	50	188	48	51	51	—2	1	1

Systems of two elements

In the tables the corrected values obtained by means of single correction (I) and of double correction (II) are given. The differences shown in the tables should be compared with those corresponding to uncorrected values (U).

Aqueous systems. See Table IV.

Acid systems. See Table V.

Systems of three elements

The results given in the tables have been corrected according to the methods mentioned above (double correction).

Aqueous systems. See Table VI.

Acid systems. See Table VII.

TABLE V

CORRECTION OF RESULTS

Interferences of two elements (acid solutions)

		Added p.p.m.		*Found p.p.m.*		*Corrected p.p.m.*		*Differences p.p.m.*		
System	*A.E.*	*I.E.*	*A.E.*	*I.E.*	*A.E.*	*(I)*	*(II)*	*(U)*	*(I)*	*(II)*
Co/Cr	Cr	200	2000	571	1792	1963	2007	—218	37	7
		200	800	442	748	777	777	—52	—23	—23
		200	200	330	196	190	190	—4	—10	—10
Mn/Cr	Cr	50	2000	99	1744	2424	2140	—256	424	140
		500	800	546	811	819	819	11	19	19
		500	200	541	272	242	233	72	42	33
Cr/Co	Co	2000	500	1552	834	600	541	334	100	41
		800	200	748	442	287	243	242	87	43
		200	50	160	181	105	54	131	55	4
Mn/Co	Co	50	500	55	504	499	499	4	—1	—1
		200	200	207	259	202	191	59	2	—9
		500	50	476	144	75	60	94	25	10
Cr/Mn	Mn	2000	500	1812	526	494	494	26	—6	—6
		2000	200	1736	231	204	203	31	4	3
		800	50	694	82	57	52	32	7	2
Co/Mn	Mn	50	500	144	476	485	485	24	15	15
		200	200	259	207	207	207	7	7	7
		200	50	228	59	52	48	9	2	—2

Correction of results obtained with samples of ferrous alloys

The results given above were obtained from samples prepared with known amounts of each one of the analysis elements. In this section some results are given that were obtained in the analysis of samples whose composition had been determined previously by chemical methods. Of the different types of steels and ferrous alloys analysed in our laboratories, only two examples are included here:

TABLE VI

CORRECTION OF RESULTS

Interferences of three elements (aqueous solutions)

		Added p.p.m.			*Found p.p.m.*			*Corrected p.p.m.*	*Differences p.p.m.*	
System	*A.E.*	*I.E.*	*I.E'.*	*A.E.*	*I.E.*	*I.E'.*	*A.E.*	*A.E.*	*(U)*	*(C)*
Co, Mn/Cr	Cr	500	200	2000	548	154	2096	1979	96	21
		200	50	800	296	51	863	793	63	7
		50	500	200	110	420	444	235	244	35
Cr, Mn/Co	Co	2000	200	500	2096	154	548	460	48	40
		800	50	200	863	51	296	231	96	31
		200	500	50	444	420	110	77	60	27
Cr, Co/Mn	Mn	2000	500	200	2096	548	154	200	—46	0
		800	200	50	863	296	51	63	1	13
		200	50	500	444	110	420	495	—80	—5

TABLE VII

CORRECTION OF RESULTS

Interferences of three elements (acid solutions)

		Added p.p.m.			*Found p.p.m.*			*Corrected p.p.m.*	*Differences p.p.m.*	
System	*A.E.*	*I.E.*	*I.E'.*	*A.E.*	*I.E.*	*I.E'.*	*A.E.*	*A.E.*	*(U)*	*(C)*
Co, Mn/Cr	Cr	500	200	2000	676	228	1912	1988	—88	—12
		200	50	800	338	72	688	762	—112	—38
		50	500	200	146	586	276	236	76	36
Cr, Mn/Co	Co	2000	200	500	1912	228	676	493	176	—7
		800	50	200	688	72	338	205	138	5
		200	500	50	276	586	146	67	96	17
Cr, Co/Mn	Mn	2000	500	200	1912	676	228	207	15	7
		800	200	50	688	338	72	53	6	3
		200	50	500	276	146	586	514	123	14

Sample A

The sample contained chromium (0.70%), manganese (0.48%) and nickel (2.46%). Nickel was extracted by means of dimethylglyoxime and chloroform in the presence of ammonium citrate. Manganese was determined by flame photometry in the presence of chromium. The results of six determinations are shown in Table VIII. The experimental values corrected according to methods previously published[1,2], gave as an average of six determinations: 0.53%.

Sample B

The sample contained chromium (4.75%), cobalt (4.90%) and manganese (0.42%). Cobalt and manganese were determined by means of six analyses by flame photometry in the presence of chromium. The results are given in Table VIII. The experimental values corrected according to methods previously published[1,2], gave as an average of six determinations: 4.36% of cobalt and 0.48% of manganese.

TABLE VIII

CORRECTED RESULTS IN THE ANALYSIS OF FERROUS ALLOYS*

Sample	*Elements*							
	Cobalt				*Manganese*			
	*Present*** %	*Found**** %	*Average* %	*Differences*	*Present*** %	*Found**** %	*Average* %	*Differences*
A	—	—	—	—	0.48	0.49 0.49 0.40 0.42 0.32 0.42	0.42	—0.06
B	4.90	4.51 5.65 4.98 5.05 4.93 5.59	5.28	0.38	0.42	0.49 0.51 0.35 0.56 0.56 0.43	0.48	0.06

* Results taken from the work of one of the authors[7].

** Determined by chemical methods.

*** Determined by flame photometry and corrected according to the method described in this paper.

DISCUSSION

Although the correction methods previously published can be applied to interference systems similar to those described in this paper[1,2], these new methods constitute a fresh advance in the correction of experimental results in systems of two elements and they also solve the difficult problem of triple interferences in systems of three elements. The corrected values are obtained from the values determined experimentally in the flame photometer, the only available values, a study of the behaviour in the flame photometer of a series of solutions of known composition having previously been carried out.

Situation of the straight lines in the graphs factor versus ponderal ratio

If we compare the situation of the graphs *factor versus ponderal ratio*, some conclusions may be drawn, as follows:

Systems of two elements

Co/Cr systems. The three straight lines are grouped more closely together for aqueous solutions. This indicates a greater interaction between both elements in acid solution. The straight line which corresponds to the intermediate concentration (800 p.p.m. of Cr) approaches $F_c = 1$ when $\log R_p = 4.0$.

Mn/Cr systems. Effects similar to those of the former system can be observed, but here a greater depression for chromium in acid solution is shown. In both types of solutions the straight line of the intermediate concentration approaches $F_c = 1$ when $\log R_p = 3.0$.

Cr/Co systems. Both types of solutions are very similar, the effects obtained with acid solutions being much more uniform. For any value of log R_p greater than 2.0 an enhancing of the experimental values can be observed (factors less than unity.)

Mn/Co systems. Similar results to those obtained with Cr/Co systems.

Cr/Mn systems. The behaviour of manganese is similar in both types of solutions. The experimental points are grouped more closely together for acid solutions. Depressions are shown especially in the case of aqueous solutions.

Co/Mn systems. As a difference between both types of solutions we may indicate that, in general, the manganese values are depressed by the cobalt in aqueous solutions, but enhanced in acid solutions. The straight line corresponding to the intermediate concentration (200 p.p.m. of Mn) maintains its slope near zero and its factors F_c approach unity at any value of the ponderal ratio, when acid solutions are considered. Its slope is positive for aqueous solutions giving a factor greater than unity for any value of log R_p greater than 2.2.

Systems of three elements

Co, Mn/Cr systems. Acid and aqueous solutions are not very similar. In both an enhancing is observed with the exception of solutions very concentrated in chromium (acid solutions).

Cr, Mn/Co systems. Both types of solution show similar behaviour. Solutions containing high concentrations of cobalt give depressed values for log R_{pm} less than 4.0.

Cr, Co/Mn systems. Only those solutions that contain small concentrations of manganese show great enhancing. The experimental points are grouped more closely together in the case of aqueous solutions.

Shape and situation of the auxiliary graphs

The shape and situation on the graph paper of the auxiliary curves used to calculate the constants m, b, m_1 and b_1 will be considered in general in a further paper and the use of these curves will be extended to several interference systems of three elements[10].

Some considerations on the results

From the results obtained with the correction methods described in this paper we find that it is convenient to carry out a double correction in systems of two elements, even if some doubly corrected values are more erroneous than those obtained on single correction.

In systems of three elements, a double correction appears to be necessary, in the majority of the cases, owing to the distortion of the concentration values caused by the presence of the other elements in the test solution.

The results obtained with samples previously analysed by chemical methods agree, within permissible limits, with those obtained by chemical procedures.

As a general rule for every study carried out on interference systems in flame photometry, it must be remembered that results of interferential effects will be reproduced if the working conditions are also reproduced. Any variation in the working conditions will require a new general review of the system, necessitating a new study of the behaviour of solutions of known composition. Even when working under the same conditions, a periodic checking of the interferential system is advisable, just as the behaviour of the standard solutions is periodically checked by us.

References p. 558

SUMMARY

The correction methods proposed by two of the authors (F.B-M. and J. R-M.), for interferential systems of two or three elements in flame photometry, have been applied to the interferential effects that occur in solutions containing chromium, cobalt and manganese, all three elements being present or combinations of two of them.

A comparison has been made of the different systems in aqueous and sulphuric acid solutions, with concentrations which varied between 50 and 500 p.p.m. of cobalt or manganese and between 200 and 2000 p.p.m. of chromium.

The correction methods that may be applied to experimental values obtained by flame photometry with these systems have been indicated. A series of examples have also been included in order to show the results obtained with prepared solutions of known concentration and with samples previously analysed by chemical methods.

Finally, the possibility of increasing the accuracy of the methods by means of a double correction has been considered.

RÉSUMÉ

Les méthodes de correction, proposées par deux des auteurs (F.B.-M. et J.R.-M.) pour l'étude des systèmes d'interférence dans la photométrie de flamme, ont été appliquées aux effets produits dans des solutions de chrome, cobalt et manganèse (systèmes de deux de ces éléments ou systèmes de tous les trois). On a comparé les systèmes en solution aqueuse et acide (acide sulfurique) avec des concentrations variables de 50 à 500 p.p.m. de cobalt et de manganèse et de 200 à 2000 p.p.m. de chrome. Les méthodes de correction, qui peuvent être appliquées aux résultats obtenus par photométrie de flamme, ont été indiquées. Des exemples sont donnés pour montrer les résultats obtenus avec des solutions préparées, de concentration connue et avec des échantillons préalablement analysés par des méthodes chimiques. Finalement, on a examiné les possibilités d'augmenter l'exactitude de la méthode par une double correction.

ZUSAMMENFASSUNG

Die von zweien der Verfasser (F.B.-M. und J.R.-M.) vorgeschlagenen Korrekturmethoden für das Studium der Interferenzsysteme zweier oder dreier Elemente bei der Flammenphotometrie wurden angewendet um eine Übersicht über die Interferenzeffekte zu geben, die in Chrom, Kobalt und Mangan (oder zwei dieser Elemente) enthaltenden Lösungen auftreten. Systeme in wässriger oder schwefelsaurer Lösung und mit Kobalt- oder Mangankonzentrationen von 50 bis 500 Teilen pro Million und Chromkonzentrationen von 200 bis 2000 Teilen pro Million wurden verglichen. Die Korrekturmethoden die man auf die photometrisch erhaltenen Versuchsergebnisse anwenden kann, wurden mitgeteilt. An Hand einer Reihe von Beispielen wurde gezeigt, welche Ergebnisse man mit hergestellten Lösungen bekannter Konzentration und mit vorher chemisch analysierten Proben erhält. Schliesslich wurde die Möglichkeit in Betracht gezogen, die Genauigkeit durch eine doppelte Korrektur zu erhöhen.

REFERENCES

[1] F. Burriel-Martí, J. Ramírez-Muñoz and M. C. Asunción-Omarrementería, *Anales real soc. españ. fís. y quím.*, B 52 (1956) 221.

[2] F. Burriel-Martí, J. Ramírez-Muñoz and M. C. Asunción-Omarrementería, *Mikrochim. Acta*, (1956) 362.

[3] J. Ramírez-Muñoz and F. Burriel-Martí, *Anales real soc. españ. fís. y quím.*, B 52 (1956) 169.

[4] F. Burriel-Martí and J. Ramírez-Muñoz, *Quím. e ind. (Bilbao)*, not yet published.

[5] F. Burriel-Martí and J. Ramírez-Muñoz, *Fotometría de llama*, Vol. I and II, Monografías de Ciencia Moderna, publ. by The High Council of Scientific Research of Spain (Consejo Superior de Investigaciones Científicas), Madrid, 1955.

[6] F. Burriel-Martí and J. Ramírez-Muñoz, *Flame Photometry. A Manual of Methods and Applications*, Elsevier Publishing Co., Amsterdam, 1957.

[7] M. C. Asunción-Omarrementería, *Doctoral Thesis*, University of Madrid, 1957.

[8] F. Burriel-Martí, J. Ramírez-Muñoz and M. C. Asunción-Omarrementería, *Inst. hierro y acero*, 9 (Spec. No. 45) (1956) 417.

[9] F. Burriel-Martí and J. Ramírez-Muñoz, *Inform. quím. anal. (Madrid)*, (in the press).

[10] F. Burriel-Martí and J. Ramírez-Muñoz, *Paper presented at the Meeting of the Spanish Society of Soil Science*, Madrid, March, 1957.

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INDIRECT FLAME PHOTOMETRIC DETERMINATION OF SULPHATE IONS*

by

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INTRODUCTION

Among the modern instrumental techniques of analysis *flame photometric* methods are widely used. These methods provide the analyst with the opportunity of making quantitative determinations of many elements for which no sufficiently rapid chemical methods were available if the accuracy and precision were to be satisfactory[1,2].

It must be pointed out that flame photometry is limited by the extent to which the elements to be determined emit radiations. If the radiations of the element are not susceptible to quantitative measurement, there is, however, still the possibility of indirect measurement, according to the so-called methods of *indirect flame photometry*.

In these indirect methods the elements or compounds to be analysed are made to react with another element which can easily be excited and determined, or else use is made of secondary effects[2].

Indirect flame photometry by difference is simple and offers ample possibilities of application to the analysis of anions whenever it is possible to find excitable elements that form precipitates (sufficiently insoluble and easy to separate by filtration or centrifugation) with the anions (chlorides, bromides, iodides, sulphates, carbonates, phosphates, etc.). Quantitative determination by difference is based on determining the amount of added element, used as background element, remaining in solution.

The indirect determination of sulphates can be carried out by flame photometry by precipitating them with barium or strontium, as the sulphates of these two elements are highly insoluble and can easily be separated by filtration or even better by centrifugation. At the same time these two elements give flame spectra of sufficient sensitivity and can easily be used for quantitative estimations.

There are not many references to the indirect determination of sulphates by flame photometry[1,2]. The determination of sulphates by this method has been achieved with biological samples. Determinations of sulphate ions in serum (after removing the phosphate ions with uranyl acetate) have been carried out by difference using barium concentrations of about 60 to 300 p.p.m.[3].

*** Paper presented at the XVth Congress of the I.U.P.A.C., Lisbon, Sept., 1956 (Section IV).**

Choice of barium and strontium as background elements

Among the elements that can be precipitated as easily separable sulphates, barium and strontium must be mentioned because of their low solubility products, *i.e.* $pP_S = 10.0$ and $pP_S = 6.40$, respectively; they are also more suitable than other elements, *e.g.* lead, for flame photometric determinations. The solubility product of lead $pP_S = 7.60$ but its photometric sensitivity $pD_{Pb} = 4.52$ as compared with the values $pD_{Ba} = 6.00$ and $pD_{Sr} = 6.00$ for the two other elements in the conditions referred to in the experimental part. In this paper we have studied the determination of sulphates by indirect methods using barium and strontium as background elements.

EXPERIMENTAL PART

Experimental conditions

Apparatus

For all work a Beckman Flame Spectrophotometer model DU No. 9200, with non-multiplier phototubes, was used.

Gases. Acetylene and oxygen.

Pressure of the gases. The following constant pressures have been used: 5 pounds per square inch and 10 pounds per square inch, respectively. The effects of variations of the gas pressures have, however, been investigated.

Slit. In each case we have tried to keep the slit as narrow as possible in order to diminish the position interference due to superposition of flame background (0.4 mm for Ba and 0.3 mm for Sr).

Instrumental sensitivity. Sensitivity selector in position 0.1 and sensitivity knob near to the position of highest sensitivity.

Phototubes. Red for Ba 873 mμ and Sr 681 mμ; *blue* for Ba 493 mμ and Sr 461 mμ.

Solutions

Chemicals. Distilled water and chemically pure products (Analytical Reagent Grade).

Stock solutions. 1000 and 500 p.p.m. of Ba and 1000 and 500 p.p.m. of Sr. Solutions of 1000 p.p.m. were prepared from the carbonate in the case of Sr, and from the chloride in that of barium. Strontium carbonate was carefully dissolved in the smallest possible quantity of 1:1 HCl, then evaporated to dryness and extracted with distilled water.

Standard solutions. The standard solutions were prepared starting from 250 p.p.m. of Ba or Sr as the highest limit, and ranged from 250 p.p.m. to 25 p.p.m.

Dilution series of the standard solutions. Dilution factors: 1/1, 1/2, 1/5 and 1/10. Aqueous series: for Ba and Sr, dilution with distilled water. Alcoholic series: for Sr only, dilution with 20% ethyl alcohol (v/v).

Background solutions. Distilled water and also 20% ethyl alcohol (v/v).

Blanks. The background solutions were used as blanks.

Spectral characteristics of barium and strontium

The following characteristics were studied: the experimental curves of the emission spectra, sensitivity, most suitable concentration ranges, influence of variation of gas pressures and spectral response of the standard solutions prepared[4].

Interferences

The interferences of various metallic elements and anionic radicals on barium and strontium were studied, as well as the influences of ethyl alcohol and hydrochloric acid.

Interferences produced by metals

It was observed that small concentrations of sodium caused a slight depression of barium radiations. These concentrations have no great effects on 100 p.p.m. of strontium, and produce only slight depressions in the case of lower concentrations of this element. Potassium in small concentrations has similar effects on both elements.

Sodium and potassium in high concentrations cause an enhancing of radiation for both elements (Figs. 1 and 2).

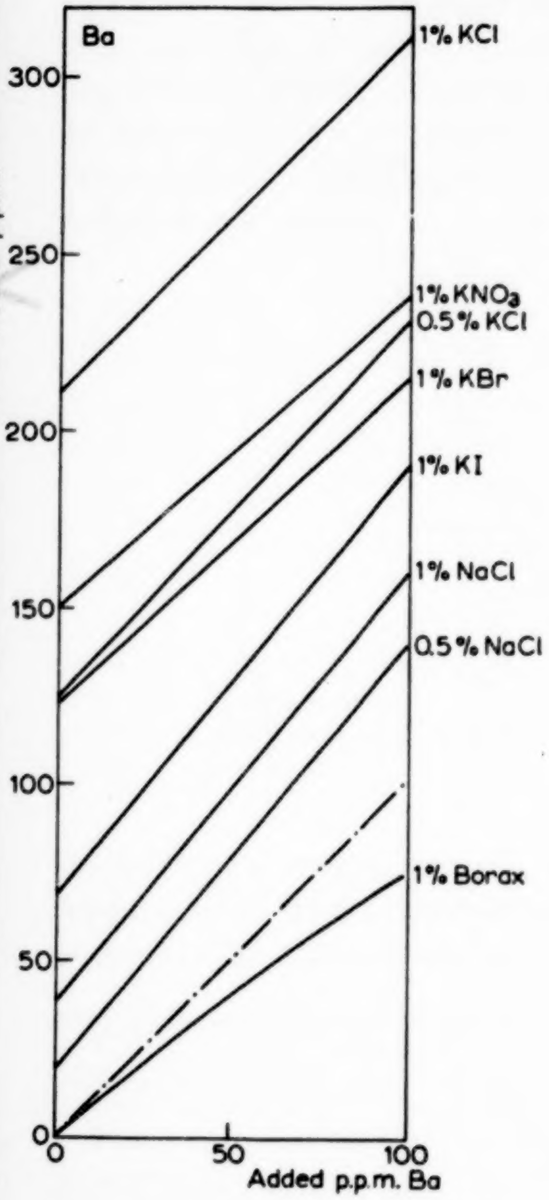

Fig. 1. Interferential effects of high salt concentrations on barium.

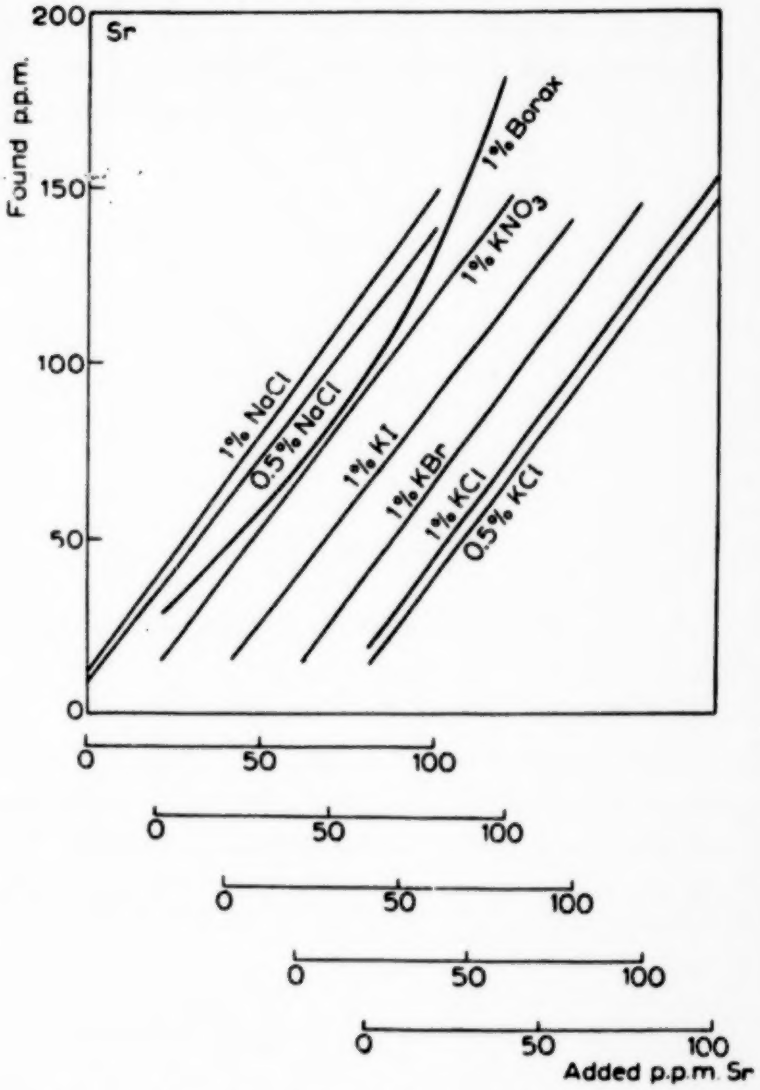

Fig. 2. Interferential effects of high salt concentrations on strontium.

Interferences produced by some anionic radicals

In Figs. 1 and 2 the effects of some sodium and potassium salts are shown besides the effects of NaCl and KCl.

Interferences produced by ethyl alcohol

The influence of alcohol appears as an enhancing of the emissions, this being higher for strontium. As it was necessary to use alcohol when preparing the precipitation series with strontium, standard solutions of this element received alcohol additions equal to those which the samples contained: 20% alcohol (v/v). See effects of ethyl alcohol on barium and strontium in Fig. 3.

Interferences produced by hydrochloric acid

The barium emission is enhanced with increasing content of hydrochloric acid from 0.05N onwards (Fig. 4).

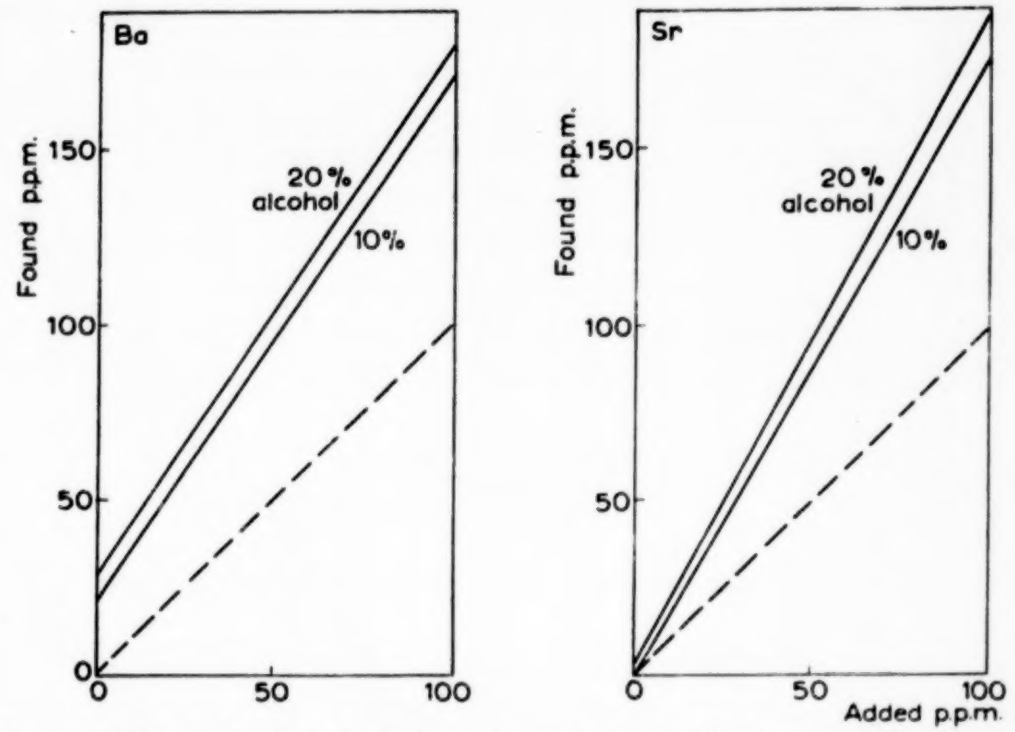

Fig. 3. Effects of ethyl alcohol on the emissions of barium and strontium.

Interferences produced by sulphate ions

The interferences of sulphate ions, the basis of the present report, were studied: (a) as interferences or effects due to *precipitation* of a fraction of the total concentration of the element used as background element, and (b) as interference through *inhibition* in the cases when no precipitation is recorded.

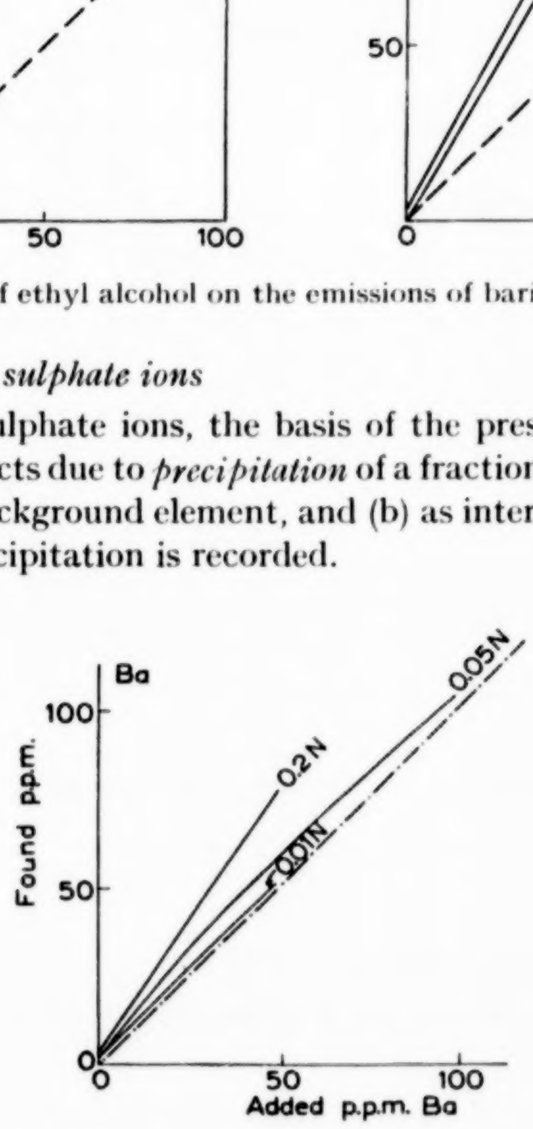

Fig. 4. Effects of the presence of HCl on the emission of barium.

Investigation of the effects of sulphate ions

Effects of sulphate ions on barium

Procedure. Aliquots of solutions containing known quantities of sulphate ion (from 0 to 70 p.p.m. after dilution up to 10 ml) are put into a centrifuge tube of 10 ml. These aliquots must be 6 ml or less. Then 4 ml of barium solution of 250 p.p.m. are added to each tube, the addition being carried out in the cold. If necessary distilled water is added immediately to give a total of 10 ml. After shaking it is left to stand overnight. The tube is then placed in the centrifuge for half an hour. The supernatant solution is drawn off and in it the concentration of residual barium is determined with the flame photometer. Tests have also been carried out using 2 and 1 ml of solutions of 250 p.p.m. of barium.

Results. See Fig. 5. The curves obtained show a slight deviation from linear proportionality. This deviation cannot be wholly ascribed to an influence of the sodium on the barium radiation, because then it would be smaller than it is. Moreover, it would be more obvious in the curves corresponding to smaller quantities of barium, because the interference ratio would then be greater. It is more likely that it is caused by adsorption of barium on the precipitate of barium sulphate.

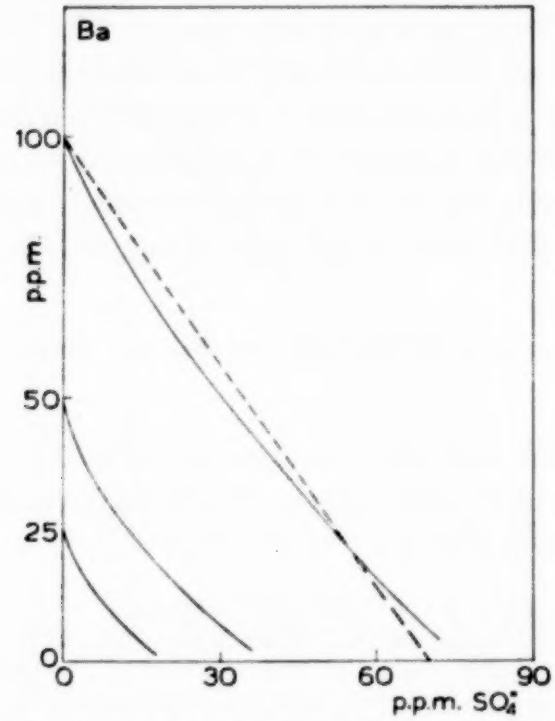

Fig. 5. Working curves, using barium as background element, for different concentration ranges.

Hot precipitation (half an hour on the steam bath) gives erroneous results due to partial evaporation.

Additions of 10 or 20% of ethyl (v/v) do not give better results, while at the same time difficulties arise due to the enhancing of the barium radiation and the risk of introducing errors by partial evaporation.

Experiments carried out in the presence of small concentrations of HCl (less than 0.05*N*) do not show any interfering effects.

Effects of sulphate ions on strontium

Procedure. The same as that described for barium.

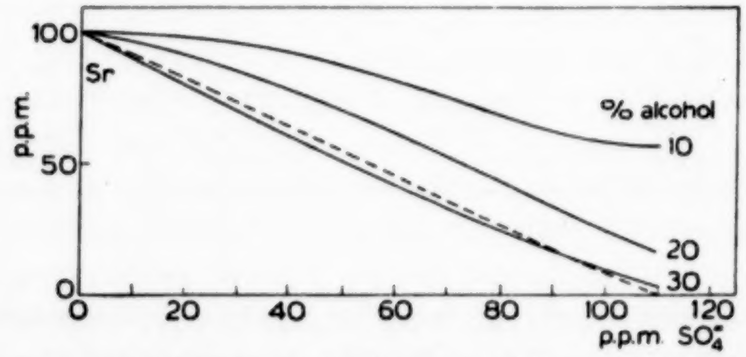

Fig. 6. Working curves using strontium as background element. The effects of various alcohol concentrations are also shown.

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Results. No precipitates were formed, but a decrease of the emission intensity was observed due to inhibition effects.

Precipitation in the presence of ethyl alcohol. The same procedure as before was used — also working in the cold — but alcohol was added to obtain 10, 20 and 30% alcohol in the total volume of 10 ml, 100 p.p.m. of strontium and from 0 to 110 p.p.m. of sulphate ion being present.

Results. More effective precipitations were obtained on increasing the quantity of alcohol present (Fig. 6), the correction of the experimental values for the exaltations produced by the presence of alcohol having been verified. The curve corresponding to 30% alcohol is very like the precipitation curve found with barium. However, this curve shows greater deviations because of a greater risk of partial evaporation. The shape of the curve corresponding to an addition of 20% ethyl alcohol with alcoholic standards is more logical, and there is less risk of evaporation.

Determination of sulphate ions by indirect flame photometry

Absence of salts

Sulphate ions in aqueous solutions containing no salts (except alkali sulphates) can be determined by any of the methods mentioned above, operating in the presence of barium or against alcoholic solutions of strontium.

Procedure with barium. The same as that described above.

Procedure with strontium. To an aliquot (not more than 4 ml) of the solution to be analysed, are added 2 ml of absolute ethyl alcohol and 4 ml of a solution of 250 p.p.m. of strontium, and then the necessary quantity of distilled water (for samples under 4 ml) to obtain a final volume of 10 ml, the additions being made in the cold. The tubes are left overnight in the cold, keeping them well closed. They are centrifuged for half an hour and the supernatant solution is compared in the flame photometer with the corresponding alcoholic standard solutions.

Working curves. In order to find the concentrations of sulphate ion in the samples, the precipitation curves mentioned above were used as working curves.

Results. See Table I.

TABLE I

SOME RESULTS OBTAINED WITH SOLUTIONS THAT DO NOT CONTAIN SALTS

Background element					
Barium p.p.m. Ba present = 100			*Strontium* p.p.m. Sr present = 100		
p.p.m. SO_4^{-2} added (b)	p.p.m. SO_4^{-2} found (a)	Differences p.p.m. (a—b)	p.p.m. SO_4^{-2} added (b')	p.p.m. SO_4^{-2} found (a')	Differences p.p.m. (a'—b')
50.0	43.5	—6.5	50.0	55.0	5.0
50.0	43.5	—6.5	50.0	54.5	4.5
50.0	44.5	—5.5	50.0	53.0	3.0
50.0	43.5	—6.5	50.0	53.0	3.0
50.0	42.5	—7.5	50.0	53.0	3.0

Presence of salts

In the presence of various salts it was found that the emissions of the elements barium and strontium were modified. For the determination of sulphate ions in the presence of salts it is therefore necessary first to correct the apparent results obtained in the flame photometer, using as correction curves those shown in Figs. 1 and 2. With the corrected experimental values one can operate as for determination of sulphate ions in the absence of salts.

However, the presence of high concentrations of a particular salt has an influence on the precipitation of the corresponding sulphates, in some cases the precipitation of strontium sulphate being prevented or the working curves of barium being greatly modified (Fig. 7).

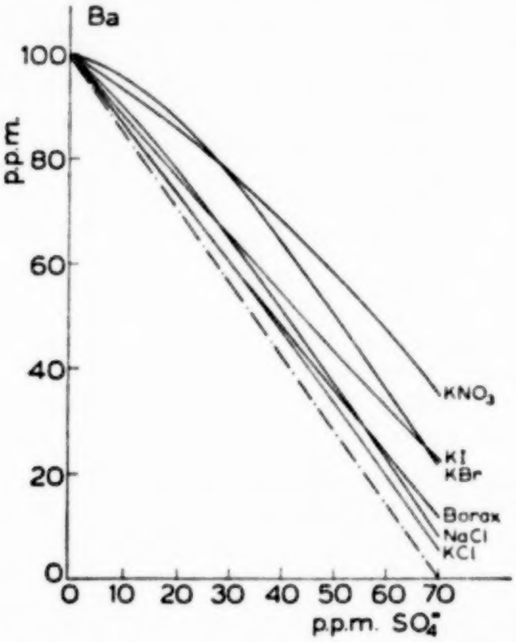

Fig. 7. Working curves, using barium, in the presence of several salts.

This fact led us in most cases not to employ strontium as background element in the determination of sulphate ions in the presence of salts. It also obliged us to make a meticulous revision of the working curves to be used in each particular case.

In order to use one correction curve of apparent values of the background element for each particular salt, it is convenient to have a constant concentration of the substance accompanying the background element. For greater simplicity, in these experiments we have used the substances in proportions of 1%. In this way it is possible to use one correction curve only for each salt and not a net of curves, which would be the most general case.

Salts not converted into sodium or potassium chloride. Solutions containing sulphate ions and 1% of the salt were investigated. It is easy to obtain this concentration starting from solutions of 2.5% of these compounds. From these solutions 4 ml were taken and finally diluted to 10 ml before centrifuging. In this case such substances as sodium chloride, potassium chloride, potassium iodide, potassium bromide, potassium nitrate, borax, etc., are found. See Table II.

Salts converted into the corresponding chlorides. In these circumstances we have to start from aliquots of *solid* compound which when treated by chemical methods and converted to the corresponding chloride would provide solutions equivalent to a 2.5% sodium or potassium solution; the procedure is then the same as that in the former section. Preliminary preparation procedures are in the most typical cases, the following; (a) Decomposition by treatment with HCl; (b) decomposition by calcination and treat-

TABLE II

SOME RESULTS IN THE PRESENCE OF SALTS

Salts present 1% solution	*p.p.m.* SO_4^{-2} *added (b)*	*p.p.m.* SO_4^{-2} *found (a)*	*Differences p.p.m. (a—b)*
NaCl	0.8	1.7	0.9
	8.0	10.2	2.2
	32.0	37.7	5.7
	64.0	66.0	2.0
KCl	0.8	0.0	—0.8
	8.0	8.5	0.5
	8.0	8.5	0.5
	32.0	28.0	—4.0
	32.0	39.7	7.7
	64.0	63.5	—0.5
KBr	32.0	34.0	2.0
	64.0	64.7	0.7
KI	0.8	1.5	0.7
	8.0	8.0	0.0
	32.0	30.7	—1.3
	64.0	64.0	0.0
KNO_3	0.8	2.0	1.2
	8.0	14.0	6.0
	32.0	32.0	0.0
	64.0	59.0	—5.0
Borax	0.8	1.5	0.7
	8.0	7.5	—0.5
	32.0	32.2	0.2
	64.0	60.0	—4.0

ment with HCl; (c) decomposition by a redox process and treatment with HCl; and (d) separation of some of the elements by a redox process and precipitation, and further treatment with HCl[4]. See Table III.

Determination of sulphate ions as impurity in chemical products

When dealing with solid products two main aspects can be considered: (a) The problem of determining the concentration of the sulphate ion impurity, for which the procedures given above can be followed, and (b) the determination of the degree of impurity of the analysed substance: its corresponding *purity factor.*

If the only impurity found experimentally is the sulphate ion, then the purity factor can be calculated supposing that the sulphate is linked to a cation of the same nature as the one forming the substance analysed.

In those cases when several impurities are found experimentally, some of them cationic, an accurate study of the *impurity balance* has to be carried out before deciding on the most convenient factor.

In Table IV some typical examples are given, the results of which have been obtained from substances whose only impurities are sulphates.

TABLE III

SOME RESULTS IN THE PRESENCE OF SALTS

Salt present 1% solution of the corresponding chlorides	*p.p.m.* SO_4^{-2} *added** *(b)*	*p.p.m.* SO_4^{-2} *found* *(a)*	*Differences p.p.m.* *(a—b)*
Na_2CO_3**	40.0	45.5	5.5
$Na_2C_2O_4$**	10.0	3.5	—7.5
	10.0	12.0	2.0
	40.0	34.5	—5.5
	40.0	46.0	6.0
$KBrO_3$***	10.0	11.0	1.0
	40.0	46.3	6.3
KIO_3***	10.0	13.0	3.0
	40.0	34.3	—5.7
$K_2Cr_2O_7$***	0.8	0.5	—0.3
	32.0	28.5	—3.5
K_2CO_3***	40.0	40.5	0.5

* To the solid samples sufficient quantities of sulphates were added to give, after conversion to the corresponding chlorides, the SO_4^{-2} concentration in the prepared test solutions as it is shown in the table.

** Converted into sodium chloride.

*** Converted into potassium chloride.

GENERAL DISCUSSION

We preferred to work in the "red" zone of the spectrum because there better *total emission/background* ratios were found, non-multiplier phototubes being used.

Absence of salts

Using either Ba or Sr as background element in ranges up to 100 p.p.m., the method described gives acceptable results. The determinations are more accurate if at the same time a blank determination with no sulphates is made, in order to correct any variation in the concentration of the background element. The examples given in Table I correspond to five samples of each type measured without this correction. Even under these unfavourable conditions the errors rarely exceed 10% working with small contents of sulphate ion (50 p.p.m. = 0.005% sulphate ion in the solution). With a blank determination, errors are kept within ± 2 and ± 3%.

Presence of salts

The results presented in Tables II, III and IV have been corrected for the fluctuations of the blanks measured in the same working period. Here the values obtained with potassium dichromate are low, due perhaps to a retention of sulphates by chromium hydroxide, as the separation of this precipitate is carried out in solutions not too rich in OH^- ions.

Influence of errors on the purity factors

The errors in the determinations of sulphate ions are reduced when the purity factors are calculated. Experimental fluctuations accumulate in the second or third figure

TABLE IV

PURITY FACTORS*

Salt	*% SO_4^{-2} present in the solid sample*	*Purity factor (calculated) (b)*	*% SO_4^{-2} found in the solid sample*	*Purity factor (experimental) (a)*	*Differences (a—b)*
KBr	0.09	0.9984	0.055	0.9990	0.0006
KI	0.05	0.9991	0.045	0.9992	0.0001
	0.09	0.9984	0.123	0.9978	−0.0006
KNO_3	0.05	0.9991	0.115	0.9979	−0.0012
Borax	0.08	0.9988	0.075	0.9989	0.0001
	0.32	0.9953	0.322	0.9953	0.0000
Na_2CO_3	0.045	0.9993	0.110	0.9984	−0.0009
	0.081	0.9988	0.070	0.9990	0.0002
$Na_2C_2O_4$	0.057	0.9992	0.00	1.0000	0.0008
	0.057	0.9992	0.055	0.9992	0.0000
	0.01	0.9999	0.065	0.9990	−0.0009
$KBrO_3$	0.063	0.9989	0.00	1.0000	0.0011
	0.112	0.9980	0.173	0.9969	−0.0011
KIO_3	0.07	0.9987	0.102	0.9982	−0.0005
	0.144	0.9974	0.117	0.9979	0.0005
$K_2Cr_2O_7$	0.008	0.9999	0.005	0.9999	0.0000
	0.32	0.9942	0.285	0.9949	0.0007
K_2CO_3	0.049	0.9991	0.085	0.9985	−0.0006

* Purity factors have been calculated on the basis of anhydrous sodium sulphate for sodium salts and anhydrous potassium sulphate for potassium salts. Sulphate concentration given as p.p.m. in the flame photometer has been converted into percentage.

after the decimal point in the fraction which expresses the percentage of sulphate. This produces variations at least in the fourth figure of the purity factor of the substance containing sulphates as impurities.

Therefore the method may be used even if the errors are about 10% in some cases, as the deviations in the factor will be about ± 0.01 to ± 0.1% or less.

In Table IV some examples are given of high contents of sulphate ion where the errors might be more significant. Even in these cases the errors rarely affect the third figure of the mentioned factor.

Limits of application

The maximum limit of sulphate concentration that can be determined is in any case conditioned by the concentration of the background element. The amount of this element not precipitated must be neither too large (greater than the most concentrated standard) nor too small, or the aliquot of background element will not be greater than the usual errors in the determination.

We fixed 70 and 110 p.p.m. of sulphate ion as the maximum limits, because we intended to apply the method to the estimation of impurities and not of macroquantities.

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Nevertheless, the minimum limit is more restricted, as it is conditioned by the precipitation itself and also because the fraction of the background element not precipitated may fluctuate within similar ranges as the blank fluctuations, which means a loss of precision.

Applications of the method

The method can be applied to the quantitative estimation of sulphate ions in dilute solutions of alkali metal sulphates and in highly concentrated solutions of alkali metal salts.

We also intend to use it for the determination of sulphates in natural waters.

In the case of salts being present we have been obliged to use the flame photometer in less advantageous conditions to determine elements in solutions which contained 100 to 10000 times greater quantities of other elements or components. However, the results obtained were acceptable for quantitative analysis.

SUMMARY

In this paper the possibilities have been studied of determining sulphate ions by indirect flame photometry by difference. Barium and strontium in constant concentrations were used as background elements. By means of the methods proposed sulphate ions can be determined in the concentration range 0 to 70 p.p.m. with barium and 0 to 110 p.p.m. with strontium. The determinations can be carried out in dilute solutions of alkali metal sulphates and sulphate ions can also be estimated in the presence of macroquantities of other compounds. This may prove useful for the quantitative estimation of sulphate as an impurity in chemical reagents. Some examples are given of the determination of the degree of purity of substances containing sulphates as impurities.

RÉSUMÉ

Les auteurs ont étudié les possibilités de dosage indirect des ions sulfuriques par photométrie de flamme, en utilisant le baryum et le strontium comme éléments de base, à concentration constante. Les méthodes proposées permettent de doser les ions sulfuriques de 0 à 70 p.p.m. et de 0 à 110 p.p.m., respectivement, en employant le baryum ou le strontium. Les dosages peuvent être effectués avec des solutions très diluées de sulfates de métaux alcalins, en présence de macroquantités d'autres ions. Il est aussi possible de déterminer quantitativement les sulfates comme impuretés dans des réactifs chimiques. Quelques exemples sont donnés.

ZUSAMMENFASSUNG

In dieser Arbeit wurde die Möglichkeit der indirekten flammenphotometrischen Bestimmung von Sulfationen erörtert; Barium und Strontium in konstanter Konzentration dienen hierbei als „Hintergrund". Mit Hilfe der vorgeschlagenen Methoden können Sulfationen mit Hilfe von Barium und Strontium resp. im Bereiche von 0 bis 75 Teilen pro Million und 0 bis 110 Teilen pro Million bestimmt werden. Die Bestimmungen können in verdünnten Lösungen der Alkalisulfate ausgeführt werden; ausserdem kann das Sulfation auch in Gegenwart grosser Mengen anderer Verbindungen bestimmt werden. Dies kann bei der quantitativen Bestimmung von Sulfat das als Verunreinigung in chemischen Reagentien auftritt, nützlich sein. Einige Beispiele für Bestimmungen des Reinheitsgrades von mit Sulfaten verunreinigten Substanzen werden angeführt.

REFERENCES

[1] F. BURRIEL-MARTÍ AND J. RAMÍREZ-MUÑOZ, *Fotometría de llama*, Monografías de Ciencia Moderna, C.S.I.C., Vols. I and II, Madrid, 1955.

[2] F. BURRIEL-MARTÍ AND J. RAMÍREZ-MUÑOZ, *Flame Photometry. A Manual of Methods and Applications*, Elsevier Publishing Co., Amsterdam, 1957.

[3] R. D. STRICKLAND AND C. M. MALONEY, *Am. J. Clin. Pathol.*, 24 (1954) 1100.

[4] M. L. REXACH – M. DE LIZARDUY, *Doctoral Thesis*, Univ. of Madrid, 1957.

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PAPER CHROMATOGRAPHY OF METAL COMPLEXES

PART III. RELATIONSHIP BETWEEN THE R_F AND THE STABILITY OF METAL COMPLEXES*

by

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In a previous paper[1] it was pointed out that the $R_M = \log(1/R_F - 1)$ value of a metal-ligand complex, MAx, can, under certain conditions, be related to the dissociation constant, pK_H, of the corresponding ligand acid in the eluant used in paper chromatography. For closely related ligands, as for example, acetic acid and its chloro derivatives, the R_M values obtained for metal-ligand compounds were found to be linear functions of pK_H. Since a linear relation exists[1] between the basic strength of a ligand, its pK_H value, and the pK of the compound, a linear relationship could be expected between R_M and the pK of some metal-ligand coördination compounds. In this paper we shall present some theoretical considerations to prove this relationship and give some applications of the equations obtained.

Considering the equilibria of two metal ions with the same complexing agent in the eluant used as solvent:

$$M' + Ax \rightarrow M'Ax \quad (1)$$

$$M'' + Ax \rightarrow M''Ax \quad (2)$$

the corresponding constants will be

$$K_1 = \frac{[M'Ax]}{[M'] \cdot [A]^x} \text{ for equilibrium 1} \quad (3)$$

$$K_2 = \frac{[M''Ax]}{[M''] \cdot [A]^x} \text{ for equilibrium 2} \quad (4)$$

Assuming as a first approximation that the empirical formulas of both metal complexes involved are the same — their identity will be proved graphically — the constant equals the ratio of the formation constants of the individual complexes as follows:

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* Presented at the Meeting of the "Société de Chimie Physique", Paris, November 1956.

$$K = \frac{K_1}{K_2} = \frac{[\mathrm{M'Ax}]\,[\mathrm{M''}]}{[\mathrm{M''Ax}]\,[\mathrm{M'}]} \qquad (5)$$

This means that it is not necessary to know the concentration of the complexing agent in the eluant since the metals are compared in the same solution.

On the other hand, according to MARTIN AND SYNGE[2], in the case of partition chromatography

$$R_F = \frac{A_L}{A_L + \alpha A_S} \qquad (6)$$

This may also be written as

$$\frac{1}{R_F} - 1 = \alpha \frac{A_S}{A_L} \qquad (7)$$

In this case, A_L and A_S are the cross sections of the mobile and stationary phases and are values dependent on the chromatographic conditions, while α = partition coefficient.

Similarly, as in the considerations given recently by LEDERER AND KERTES[3] for the case of partition chromatography, α is proportional to MAx/M, and from equations 5 and 7 we have

$$\log K = \log K_1 - \log K_2 = \log \alpha_1 - \log \alpha_2 \qquad (8)$$

Since only R_F can be measured directly, equation (8) must be rewritten as

$$\log K_1 - \log K_2 = \log (1/R_{F_1} - 1) + \log A_L/A_S - \log (1/R_{F_2} - 1) - \log A_L/A_S \qquad (9)$$

BATE-SMITH AND WESTALL[4] introduced the term

$$R_M = \log (1/R_F - 1) \qquad (10)$$

Hence combining equations 9 and 10, we have

$$\mathrm{p}K_1 - \mathrm{p}K_2 = R_{M_1} - R_{M_2} \qquad (11)$$

or

$$\triangle \mathrm{p}K_n = \triangle R_{M_n} \qquad (12)$$

This means that as long as identical complexes of two metal ions with the same complexing agent are formed, $\triangle R_M$ and consequently $\triangle \mathrm{p}K$ must be constant and independent of the concentration of the complexing agent and dependent only on the chromatographic conditions used.

SOME APPLICATIONS OF EQUATION (12)

We plotted the R_M values of various metal-ligand coördination compounds, chromatographed under identical and homogeneous[5] conditions, versus the negative log-

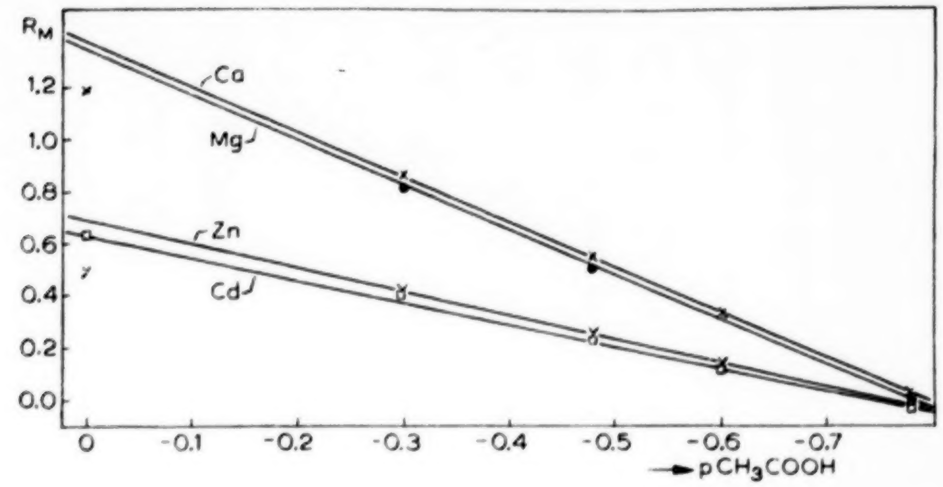

Fig. 1. R_M values of metal acetates plotted against pCH$_3$COO for various cations.

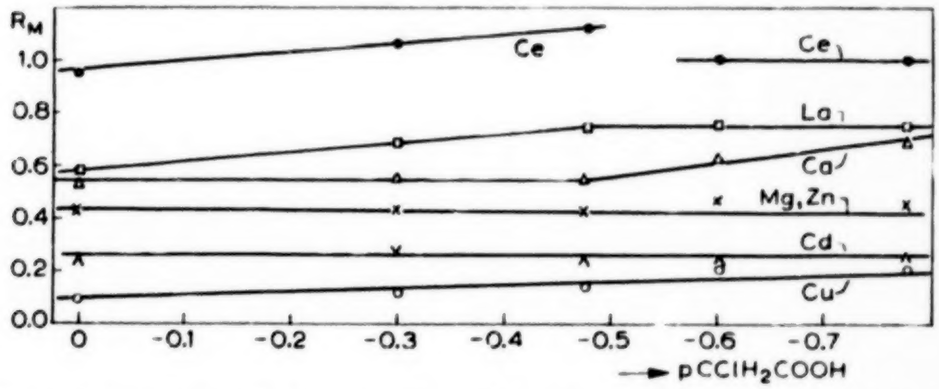

Fig. 2. R_M values of metal monochloroacetates plotted against pCH$_2$ClCOO for various cations.

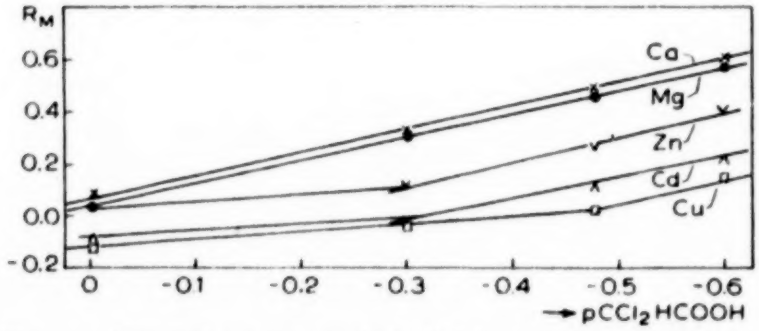

Fig. 3. R_M values of metal dichloroacetates plotted against pCHCl$_2$COO for various cations.

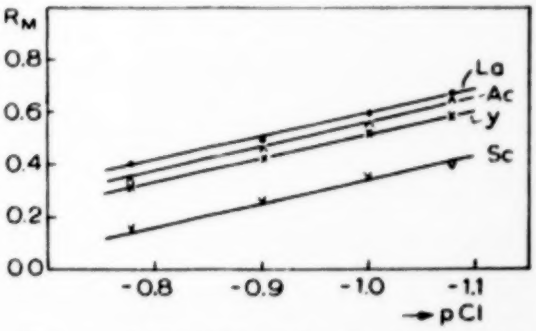

Fig. 4. R_M values of metal chloride coördination compounds plotted against pCl for various cations.

arithm of the normalites of the complexant — pAx — in the eluant. In numerous cases straight lines were obtained for a number of cations. These straight lines were even parallel in many cases where cations with similar chemical properties were examined. Examples are given in Figs. 1-6 for various cations with different complexants. In Fig. 1 the R_M values of Ca, Mg, Zn and Cd acetates[1] are plotted against pCH$_3$COO. The curve for Cu nearly overlaps that of Zn and is therefore not plotted. The values obtained in the eluant containing 1 N acetic acid lie well below the lines. In Fig. 2 the R_M values for a number of cation monochloroacetates[1] are given. Fig. 3 shows the curves for these cations as their dichloroacetates[1]. In Fig. 4 the values of some

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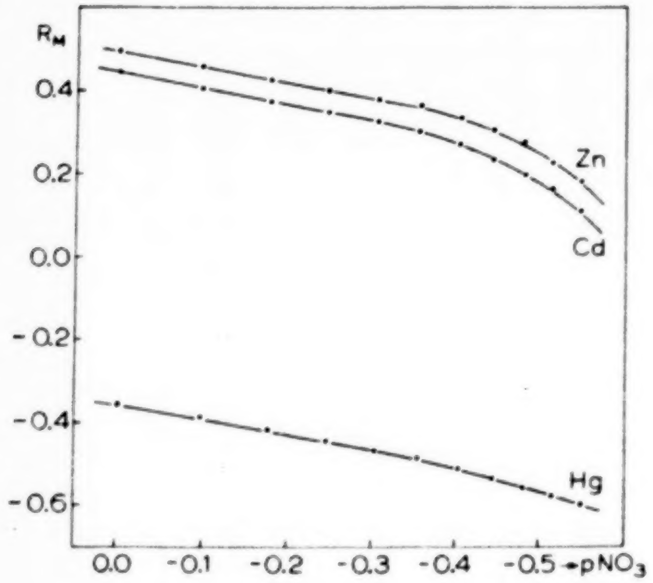

Fig. 5. R_M values of zinc, cadmium and mercury nitrates plotted against pNO$_3$ in butanol.

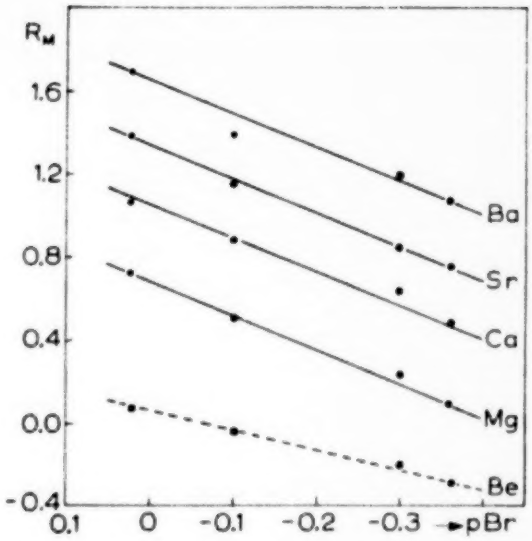

Fig. 6. R_M values of alkaline earth bromides plotted against pBr in butanol.

rare elements are plotted against the negative logarithm of the concentration of hydrochloric acid in butanol[6]. Fig. 5 represents the curves of Zn, Cd and Hg in different concentrations of nitric acid in butanol[7]. Fig. 6 shows the curves of alkaline earths obtained in hydrobromic acid-butanol mixtures[8].

In the case where R_M values of two or more metal complexes chromatographed on the same sheet of paper give parallel straight lines when plotted against the pAx of the complexant in the eluting solvent, equation (12) is valid. This means that the cations investigated form complexes with identical cation to ligand ratios. In such cases the determination of the R_M values allows the calculation of pK of one of the complexes, provided the other is known. If two or more cations under the above conditions give non-parallel straight lines, though the formation of complexes is individual, the stoichiometric composition of the metal-ligand coördination compounds remains constant during the variation in the composition of the eluant used. For example, Zn, Cd and Hg, as shown in Fig. 5, formed stoichiometrically identical nitrato-butanol-aqueous solvated complexes up to approximately 2.5N nitric acid in butanol. From this point on, the same cations behave differently. It is probable that in the case of Zn and Cd, where no straight lines were obtained, the overall formula of the complexes changes with varying composition of the eluant. The composition of the dichloroacetates of Ca, Mg, Zn, Cd and Cu, as shown in Fig. 3, is identical only at higher concentration of the complexant acid in the eluant.

It should be added, that R_M values of metallic complexes from chromatographic experiments that were carried out under non-homogeneous conditions[5] gave no straight lines when plotted versus the negative logarithm of the normalities of the complexant acid in the eluant.

ACKNOWLEDGEMENT

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SUMMARY

It is shown that the R_F values can be related to the stability constants of the corresponding metal-ligand coördination compounds. The relationship has been applied to prove graphically the stoichiometric identity of two or more complexes formed by paper chromatography in a given system.

RÉSUMÉ

On démontre que les valeurs R_F peuvent être reliées aux constantes de stabilité du composé métallique à liaison de coordination correspondant. La relation est appliquée à prouver graphiquement l'identité stoechiométrique de deux ou davantage de complexes formés, par chromatographie sur papier dans un système donné.

ZUSAMMENFASSUNG

Es wird gezeigt, dass die R_F-Werte mit den Beständigkeitskonstanten der entsprechenden Metall-Komplexverbindungen in Verbindung gebracht werden können. Das Verhältnis zwischen diesen Grössen wurde angewendet um graphisch die Identität zweier oder mehrerer durch Papierchromatographie in einem gegebenen System gebildeter Komplexverbindungen zu beweisen.

REFERENCES

[1] A. S. KERTES, *J. chim. phys.*, 54 (1957) 117; *Research* (London), 1957, in the press.

[2] A. J. P. MARTIN AND R. L. M. SYNGE, *Biochem. J.*, 35 (1941) 358.

[3] M. LEDERER AND S. KERTES, *Anal. Chim. Acta*, 15 (1956) 226.

[4] E. C. BATE-SMITH AND R. G. WESTALL, *Biochim. et Biophys. Acta*, 4 (1950) 427.

[5] A. S. KERTES, *Anal. Chim. Acta*, 17 (1957) 469.

[6] R. G. DE CARVALHO, *Anal. Chim. Acta*, 16 (1957) 555.

[7] C. BERGAMINI AND A. ROVAI, *Anal. Chim. Acta*, 15 (1956) 43.

[8] S. KERTES AND M. LEDERER, *Anal. Chim. Acta*, 15 (1956) 543.

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THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

PART IV. THE NITRONAPHTHYLAMINES AS FLUORIMETRIC REAGENTS FOR STANNOUS TIN

by

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INTRODUCTION

It has been shown that four nitroaminonaphthalene monosulphonic acids can be used as fluorimetric reagents for the determination of stannous tin[1,2,3]. Initial experiments indicate that 6-nitro-2-aminonaphthalene-8-sulphonic acid is the most sensitive of the four reagents. In determining the influence of the orientation of the nitro-group upon the sensitivity of test, it has been found that the nitronaphthylamines are of use in the estimation of stannous tin. For maximum sensitivity of test with the nitronaphthylamines, the presence of strong HCl is necessary, whereas with the corresponding nitroaminonaphthalene monosulphonic acids, the reaction is performed in aqueous media.

Spots of aqueous solutions of 47 metallic salts were placed on Whatman 3MM chromatographic paper and treated separately with a 1% solution of each of the nitronaphthylamines in 50/50 v/v absolute alcohol/10N HCl. Under these conditions, stannous tin alone fluoresced when viewed under ultraviolet light, after quenching of any previous fluorescence by treatment with 15N NH_4OH. The colour of the fluorescence was found to vary with the position of the nitro-group in the naphthylamine nucleus.

EXPERIMENTAL

Synthesis of reagents

The preparation of the nitronaphthylamines has been adequately reviewed by HODGSON AND HATHWAY[4], the methods of synthesis used in this paper being abstracted from their publication[4].

Spot test procedure

Approximately 0.02 ml of 0.1 M solutions of 47 ions were placed on Whatman 3 MM chromatographic paper by means of a platinum loop, air-dried for 30 minutes, sprayed with the described reagent, air-dried and examined for fluorescence under ultraviolet light. The paper was then sprayed with 15N NH_4OH and, after drying, again examined under U.V. light for any quenching of the previous fluorescence.

RESULTS

The reagents used are listed in Table I. The results obtained are shown in Table II.

TABLE I

REAGENTS FOR TESTS

Reagent No.	*Reagent (1% w/v solution in 50/50 v/v alcohol/10N HCl)*
1	2-Nitro-1-naphthylamine
2	3-Nitro-1-naphthylamine
3	4-Nitro-1-naphthylamine
4	5-Nitro-1-naphthylamine
5	6-Nitro-1-naphthylamine
6	7-Nitro-1-naphthylamine
7	8-Nitro-1-naphthylamine
8	1-Nitro-2-naphthylamine
9	4-Nitro-2-naphthylamine
10	5-Nitro-2-naphthylamine
11	6-Nitro-2-naphthylamine
12	7-Nitro-2-naphthylamine
13	8-Nitro-2-naphthylamine

Effect of acid upon the intensity of fluorescence

A series of experiments was performed with stannous tin, using:

(a) 1% w/v solutions of the nitronaphthylamines in absolute alcohol,

and (b) 1% w/v solutions of the nitronaphthylamines in 50/50 v/v absolute alcohol/10N HCl

in order to examine the effect of acid upon the sensitivity of the test. The results of the experiments are shown in Table III.

TABLE II

FLUORESCENCE OBTAINED ON SPRAYING SPOTS OF IONS WITH VARIOUS REAGENTS BEFORE (B) AND AFTER (A) QUENCHING WITH 15*N* NH_4OH

Ion	*Reagent number*																									
	1		*2*		*3*		*4*		*5*		*6*		*7*		*8*		*9*		*10*		*11*		*12*		*13*	
	B	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*	*A*
Au^{+3}																					F(s)					
Hg^{+}			F				F		F		F		F				F		F		F		F		F	
Hg^{+2}			F				F(s)		F		F						F		F		F		F		F	
Al^{+3}					F(s)	F(s)																				
Ce^{+3}			F								F		F				F		F						F	
Ce^{+4}							F(s)	F(s)					F						F		F					
Ga^{+3}			F				F		F		F		F				F		F		F		F		F	
In^{+3}			F				F		F		F		F				F		F		F		F		F	
Tl^{+}			F				F				F		F				F		F		F				F	
Tl^{+3}			F				F				F		F				F		F		F				F	
Ti^{+4}			F				F		F		F		F				F		F		F		F		F	
Zr^{+4}			F				F		F		F		F				F		F		F		F		F	
Sn^{+2}	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F	F
Sn^{+4}			F				F				F		F				F		F		F				F	
VO_2^{+2}			F		F(s)	F(s)					F		F				F		F		F				F	
As^{+3}									F														F			
Sb^{+3}			F				F				F		F				F		F		F				F	
Bi^{+3}			F				F				F		F				F		F		F				F	
Cr^{+3}			F				F				F		F				F		F		F				F	
UO_2^{+2}					F										F											
Fe^{+2}							F	F(s)																		
Fe^{+3}																			F							
Pt^{+2}			F								F		F				F		F		F				F	

Other ions tested included Li^{+}, Na^{+}, K^{+}, Cu^{+2}, Ag^{+}, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, La^{+3}, Th^{+4}, Pb^{+2}, VO_3^{-}, As^{+5}, Cr^{+6}, Mo^{+6}, W^{+6}, Te^{+6}, Mn^{+2}, Co^{+2}, Ni^{+2}.

B = Before quenching with 15*N* NH_4OH.
A = After ,, ,, ,, ,,
F = Fluorescence.
F(s) = Slight fluorescence.

TABLE III

EFFECT OF ACID UPON THE INTENSITY OF THE FLUORESCENCE

Reagent	*Reaction with Sn^{+2}*		*Reagent*	*Reaction with Sn^{+2}*	
Series I (1% w/v in alcohol)	*Before quenching*	*After quenching*	*Series II (1% w/v in 50/50 v/v alcohol/10N HCl)*	*Before quenching*	*After quenching*
2-Nitro-1-naphthylamine	W.F.	W.F.	2-Nitro-1-naphthylamine	S.F.	S.F.
3-Nitro-1-naphthylamine	W.F.	W.F.	3-Nitro-1-naphthylamine	S.F.	S.F.
4-Nitro-1-naphthylamine	W.F.	W.F.	4-Nitro-1-naphthylamine	F.	F.
5-Nitro-1-naphthylamine	W.F.	W.F.	5-Nitro-1-naphthylamine	S.F.	S.F.
6-Nitro-1-naphthylamine	W.F.	W.F.	6-Nitro-1-naphthylamine	S.F.	S.F.
7-Nitro-1-naphthylamine	W.F.	W.F.	7-Nitro-1-naphthylamine	F.	F.
8-Nitro-1-naphthylamine	N.F.	N.F.	8-Nitro-1-naphthylamine	F.	F.
1-Nitro-2-naphthylamine	W.F.	W.F.	1-Nitro-2-naphthylamine	S.F.	S.F.
4-Nitro-2-naphthylamine	W.F.	W.F.	4-Nitro-2-naphthylamine	F.	F.
5-Nitro-2-naphthylamine	S.F.	S.F.	5-Nitro-2-naphthylamine	V.S.F.	V.S.F.
6-Nitro-2-naphthylamine	S.F.	S.F.	6-Nitro-2-naphthylamine	V.S.F.	V.S.F.
7-Nitro-2-naphthylamine	W.F.	W.F.	7-Nitro-2-naphthylamine	S.F.	S.F.
8-Nitro-2-naphthylamine	F.	F.	8-Nitro-2-naphthylamine	S.F.	S.F.

V.S.F. = Very strong fluorescence.
S.F. = Strong fluorescence.
F. = Fluorescence.
W.F. = Weak fluorescence.
N.F. = No fluorescence.

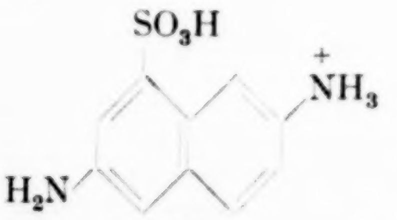
The data indicate that the presence of strong hydrochloric acid is essential for maximum fluorescence with stannous tin, when the nitronaphthylamines are used as reagents.

Sensitivity tests

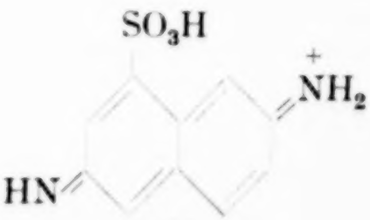
Sensitivity tests for stannous tin were performed in the presence of hypophosphorous acid as described in a previous communication[3]. All reagents were capable of detecting approximately 10^{-7} g stannous tin, although reagent numbers 10 and 11 gave the most intense fluorescence of the series. In general, the nitro derivatives of 2-naphthylamine yielded more intense fluorescence than the corresponding derivatives of 1-naphthylamine. Blank tests were performed with 2% hypophosphorous acid and no fluorescence was observed under these conditions. Even Fe^{+2} in the presence of hypophosphorous acid yielded no fluorescence with the above reagents under the conditions of test.

DISCUSSION

Evidence presented in earlier papers[1,3] of this series indicates that the fluorescence exhibited by the nitroaminonaphthalene monosulphonic acids with stannous tin is due to the excited state of the naphthyl ammonium ion (I) and not the corresponding imino form (II).



(I)



(II)

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This theory is substantiated by the results obtained when the nitronaphthylamines are used as reagents in this test. Each of the thirteen available nitronaphthylamines yields an intense blue fluorescence with stannous tin. If conjugative effects were of importance in determining the species responsible for the fluorescence, then those nitronaphthylamines, where structures such as (II) are not possible, would not be expected to react with tin under the conditions of test. It has been found that even the *meta* nitro substituted naphthylamines (*viz.* 3,1-and 4,2-compounds) exhibit no diminution in sensitivity of reaction when compared with the standard reagent 6-nitro-2-aminonaphthalene-8-sulphonic acid.

From the results of these experiments, it is now possible to predict that all nitroaminonaphthalene sulphonic acids will give a fluorimetric test with stannous tin.

The advantage of using the nitroaminonaphthalene monosulphonic acids as reagents is that they can be sprayed as aqueous solutions whereas the nitronaphthylamines require the presence of concentrated hydrochloric acid in the alcoholic solution to ensure that complete reduction of the nitro-group occurs.

ACKNOWLEDGEMENT

The authors wish to thank Dr. A. Bryson for some of the nitronaphthylamine preparations.

SUMMARY

Thirteen of the theoretically possible fourteen nitronaphthylamines have been tested and found to be of use as fluorimetric reagents for stannous tin. The presence of strong hydrochloric acid in the reagent solution is necessary for maximum sensitivity of test. This indicates that the nitronaphthylamines are not as versatile as their corresponding nitroaminonaphthalene monosulphonic acids as reagents for tin. Present evidence confirms the original postulate that the species responsible for the fluorescence is the excited state of the naphthyl ammonium ion.

RÉSUMÉ

Treize des quatorze nitronaphtylamines théoriquement existantes ont été essayées et reconnues d'un bon usage comme réactifs fluorimétriques pour l'étain (II). La présence d'acide chlorhydrique concentré dans la solution réactive est nécessaire pour obtenir le maximum de sensibilité de la réaction. Ceci indique que les nitronaphtylamines ne sont pas aussi versatiles que les acides nitroaminonaphtalène monosulfoniques correspondants, comme réactifs de l'étain.

La présente évidence confirme le postulat de départ que le spécifique responsable de la fluorescence est l'ion naphtyl-ammonium à l'état d'excitation.

ZUSAMMENFASSUNG

Dreizehn von den vierzehn theoretisch möglichen Nitronaphtylaminen wurden geprüft und es wurde festgestellt dass sie als fluorimetrische Reagenzien für zweiwertiges Zinn nützlich sind. Die Gegenwart von starker Salzsäure in der Reagenzlösung ist notwendig um eine maximale Empfindlichkeit der Reaktion zu gewährleisten. Dies zeigt dass die Nitronaphtylamine als Zinnreagenzien nicht vielfältig verwendet werden können wie die entsprechenden Nitroaminonaphtalinmonosulfosäuren. Die Annahme wird bestätigt, dass das Naphtylammonium-Ion im erregten Zustand für die Fluoreszenz verantwortlich ist.

REFERENCES

[1] J. R. A. Anderson and J. L. Garnett, *Anal. Chim. Acta*, 8 (1953) 393.
[2] J. R. A. Anderson and S. Lenzer-Lowy, *Anal. Chim. Acta*, 15 (1956) 246.
[3] J. R. A. Anderson and J. L. Garnett, *Anal. Chim. Acta*, 17 (1957) 452.
[4] H. H. Hodgson and D. E. Hathway, *J. Soc. Dyers Colourists*, 63 (1947) 231.

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THE COMPOUNDS OF GOLD AND PALLADIUM WITH RUBEANIC ACID

COMPOSITION, STRUCTURE AND ANALYTICAL USE

by

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INTRODUCTION

The reactions of rubeanic acid with gold, palladium and platinum have until now been studied on a rather qualitative basis for spot test purposes. The compositions of the compounds obtained are not known with certainty. Nothing has previously been reported about the existence and composition of the gold compounds. A palladium compound has been cited by FEIGL as having the composition $PdRub_4$(?)[1].

It was our aim to use the heterometric method for studying the nature and composition of the compounds formed at various pH's, and so investigate how far the compounds obtained are suitable for the heterometric determination of the above metals. The reaction with platinum proceeded very slowly and was therefore not suitable for study. The results of this investigation show that both gold and palladium form several well-defined insoluble compounds with rubeanic acid, some of which are suitable for the quantitative heterometric determination of these metals.

EXPERIMENTAL

Apparatus and procedure

The same working conditions were observed as in previous heterometric investigations[2]. A brie discussion of the fundamentals of heterometry has already appeared[3]. The temperature during th titrations was 20° C and was controlled thermostatically, while the rate of stirring, which was high was regulated electronically.

Reagents

The *palladium chloride* was a Fisher dry purified reagent. A 0.004*M* solution was prepared. This solution contained in addition HCl in a concentration of 0.04*M*.

Gold chloride brown, $HAuCl_4 \cdot 3H_2O$, BDH Lab. reagent was used. Of this reagent 1 g was dissolved in 500 ml aqueous solution containing in addition 25 ml *M* HCl. The final solution was approximately 0.005*M* $HAuCl_4$ (0.05*M* HCl).

The *platinum chloride* was a Johnstone Matthews H_2PtCl_6 reagent. 1 g reagent was dissolved in 500 ml aqueous solution. The solution was approximately 0.004*M*.

The *rubeanic acid* $(CSNH_2)_2$, dithioxamide, was an Eastman Kodak reagent for chemical purposes. A 0.004*M* stock solution was prepared in 95% alcohol. The solution was then diluted in water to give approximately a 50% alcoholic solution of rubeanic acid. The titrations were always carried out with the 50% alcoholic solution.

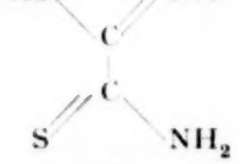
Since the properties of rubeanic acid indicate the presence of one or two HS-groups, we assume that it reacts either partly or entirely in a tautomeric form, having either one HS-group, as in:

TABLE I

Composition: *a* ml reagents + (20—*a*) H_2O +

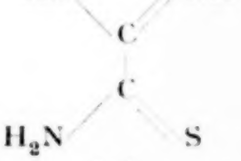
Expt. No.	*Reagents*
1	5 ml 0.002*M* $AuCl_3$ + 1 ml *M* HNO_3
2	5 ,, ,, ,, + 3 ,, ,, ,,
3	5 ,, ,, ,, + 2 ,, ,, CH_3COOH + 1.5 ml 0.1*M* CH_3COONa
4	5 ,, ,, ,, + 2 ,, ,, ,, + 1.5 ,, ,,
5	5 ,, ,, ,, + 2 ,, ,, ,, + 1.5 ,, ,, + 2 ml 2*M* NH_4NO_3
6	5 ,, ,, ,, + 2 ,, ,, ,, + 1.5 ,, ,, + 2 ,, ,, ,,
7	5 ,, ,, ,, + 2 ,, ,, ,, + 2 ml *M* CH_3COONa + 1 ml *M* NH_4Cl
8	5 ,, ,, ,, + 2 ,, ,, ,, + 2 ,, ,, ,,
9	5 ,, ,, ,, + 2 ,, *M* CH_3COONa
10	5 ,, ,, ,, + 0.5 ml conc. NH_4OH + 1 ml 2*M* NH_4NO_3
11	5 ,, ,, ,, + 0.5 ,, ,, ,, + 1 ,, 2,, NH_4Cl
12	3 ,, 0.004*M* Rub. + 4 ml 0.2*M* Na_2HPO_4
13	5 ,, 0.002*M* $AuCl_3$ + 0.5 ml conc. NH_4OH + 1 ml 2*M* NH_4NO_3
14a	5 ,, ,, ,, + 10 ml 0.1*M* $Na_4B_2O_7$
14b	5 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ml 0.2*M* Na_2EDTA
14c	5 ,, ,, ,, + 0.5 ,, ,, ,, + 1 ml *M* KCN
15	5 ,, 0.002*M* $PdCl_2$ + 0.5 ,, *M* HNO_3 + 5 ml 0.1*M* NaCl
16	5 ,, ,, ,, + 0.5 ,, ,, H_2SO_4 + 5 ,, 0.1,, NH_4Cl
17	5 ,, ,, ,, + 3 ,, ,, HNO_3 + 5 ,, 0.1,, ,,
18	5 ,, ,, ,, + 0.5 ,, ,, ,, + 5 ,, 0.1,, ,,
19	5 ,, ,, ,, + 1 ,, ,, ,, + 5 ,, *M* ,,
20	5 ,, ,, ,, + 3 ml *M* CH_3COOH + 1.5 ml 0.1*M* CH_3COONa + 0.5 ml *M* NH_4Cl
21	5 ,, 0.002*M* Rub. + 2 ,, ,, ,, + 1.5 ,, ,, ,, + 1 ,, ,, ,,
22	5 ,, ,, ,, + 2 ,, ,, ,, + 1.5 ,, ,, ,,
23	5 ,, ,, $PdCl_2$ + 2 ,, ,, CH_3COONa + 3 ml *M* NH_4NO_3
24	5 ,, ,, ,, + 2 ,, ,, ,, + 1 ,, ,, NH_4Cl
25	5 ,, ,, ,, + 2 ,, ,, ,, + 3 ,, ,, ,,
26	5 ,, ,, ,, + 4 ,, 0.2*M* Na_2HPO_4
27	5 ,, ,, ,, + 4 ,, ,, ,, + 3 ml *M* NH_4Cl

* c.p. = critical point; h = horizontal line.



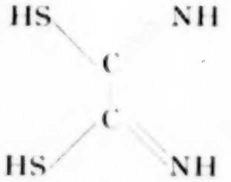
(a)

or



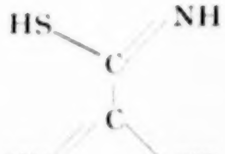
(a′)

or two such HS-groups, as in:



(b)

or



(b′)

Because of these circumstances it is very difficult to assign final structures to the various rubeanates. On the one hand, by the action of metals with reagents containing the HS-group alone, insoluble mercapto compounds are obtained, while, on the other hand, since both gold and palladium give very stable complexes with ammonia, the participation of the nitrogen in the formation of the complex compounds seems to be a very reasonable assumption. All the compounds obtained have an intense brownish-red colour and are insoluble.

x ml *b M* titrant. Temp. = 20°C.

pH of the solution	*Titrant*				*Compound obtained at*		*Optical density value at*		*Titration time in min at*	
	name	*molarity*	*ml used at*							
			1st c.p.	*2nd c.p.*	*1st c.p.*	*2nd c.p.*	*1st c.p.*	*2nd c.p.*	*1st c.p.*	*2nd c.p.*
∼ 1	Rub. ac.	0.0025	4.01h		Au_1R_1		0.53		35	
∼ 1	,,	0.004	2.53h		,,		0.54		46	
∼ 3	,,	0.004	2.45h		,,		0.34		16	
∼ 3	,,	0.0025	3.87h		,,		0.47		23	
∼ 3	,,	0.0025	3.98h		,,		0.48		27	
∼ 3	,,	0.004	2.52h		,,		0.47		26	
∼ 5	,,	0.004	3.62h		Au_2R_3		0.45		46	
∼ 5	,,	0.004	3.70h		,,		0.53		42	
∼ 7	,,	0.004	4.05h		,,		0.60		35	
∼10	,,	0.00166	3.60h		Au_3R_2		0.54		15	
∼10	,,	0.00166	3.65h		,,		0.54		17	
∼ 8	$AuCl_3$	0.004	4.65h		,,		0.58		58	
∼10	Rub. ac.	0.004	1.66h		,,		0.63		13	
∼10	,,	0.004	no precip.							
∼10	,,	0.004	,, ,,							
∼10	,,	0.004	,, ,,							
∼ 1	,,	0.00166	3.9h		Pd_3R_2		0.60		17	
∼ 1	,,	0.0025	2.67h		,,		0.64		13	
∼ 1	,,	0.0025	2.54h	4.35h	,,	Pd_1R_1	0.62	0.72	12	36
∼ 1	,,	0.0025	2.57h		,,		0.56		13	
∼ 1	,,	0.0025	4.1h		Pd_1R_1		0.48		92	
∼ 3	,,	0.0025	2.63	4h	Pd_3R_2	Pd_1R_1	0.37	0.46	20	58
∼ 3	$PdCl_2$	0.004	3.78		,,		0.41		51	
∼ 3	,,	0.004	2.63h		Pd_1R_1		0.44		38	
∼ 7	Rub. ac.	0.004	4.9h		Pd_1R_2		0.70		111	
∼ 7	,,	0.0066	2.2	3.1h	Pd_2R_3	Pd_2R_2	0.63	0.63	9	111
∼ 7	,,	0.0066	2.5h		,,		0.54		49	
∼ 8	,,	0.0066	2.4h		,,		0.69		65	
∼ 8	,,	0.0066	2.42h		,,		0.83		66	

Reactions between rubeanic acid and cations are known which lead to the decomposition of the rubeanic acid and the formation of sulphides. Thus a heterometric study of the reaction between silver and rubeanic acid in ammoniacal solution showed that silver sulphide was formed quantitatively (unpublished results).

RESULTS

Composition

We present in Table I the results obtained in a series of experiments. The course of the reaction of certain experiments is shown in Figs. 1 and 2. The composition of the compounds, calculated from the critical points (= breaks) in the curves, are also given in the table. Most of the titrations were carried out with rubeanic acid as titrant. A few reverse titrations were also carried out. The titrations were carried out at the following pH's: 1, 3, 4.7, 7, 8 and ∼ 10. From the curves obtained *three* critical points were obtained with each metal studied.

Thus gold gave the following compounds: at pH 1-3, the compound Au_1R_1; at pH 5-7, Au_2R_3; and at pH 8-10, Au_3R_2.

All three compounds were light brown in colour and insoluble in water.

It is remarkable that palladium compounds of similar composition were also obtained, but the pH ranges in which they were formed were different in the two cases.

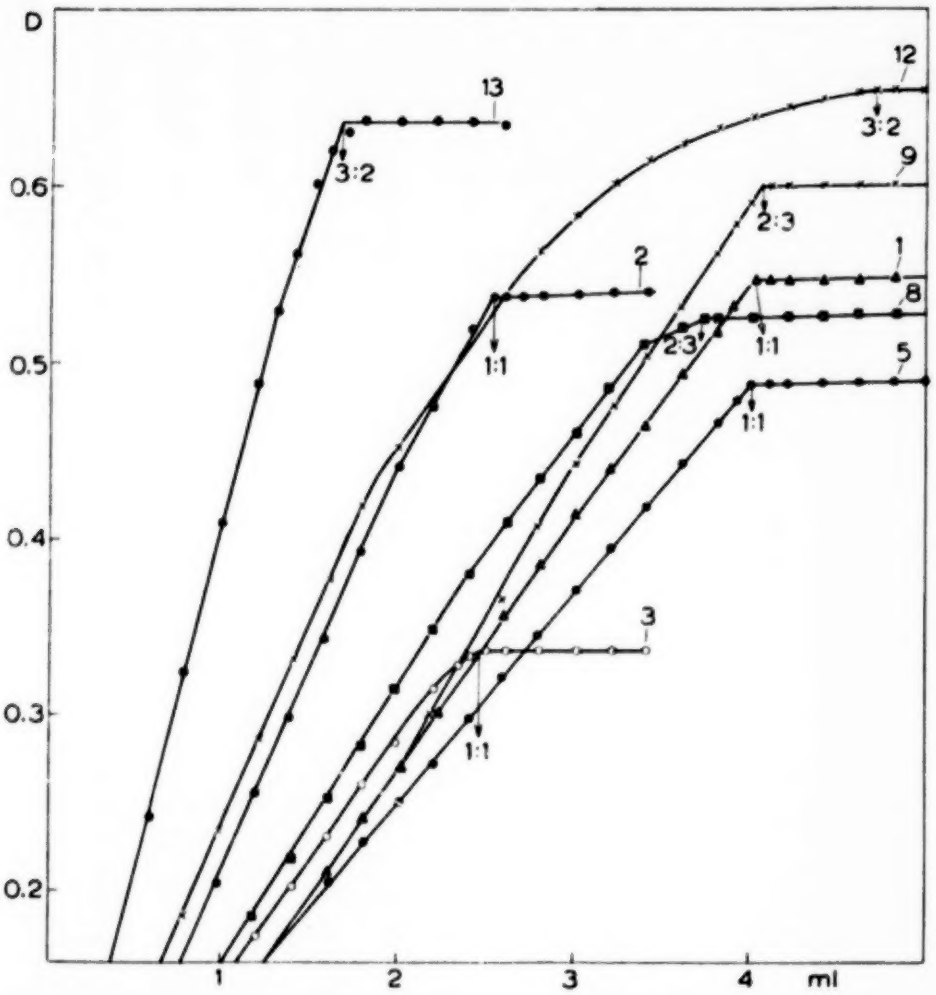


Fig. 1. Titrations of gold chloride or palladium chloride solutions with rubeanic acid.

Thus palladium gave the following compounds: at pH 1-3, Pd_3R_2, which was, in certain cases, transformed on the addition of an excess of rubeanic acid into Pd_1R_1. At pH 7-8 the compound Pd_2R_3 was obtained and, in certain cases, this was transformed, by the addition of an excess of rubeanic acid, into Pd_1R_2.

ANALYTICAL ASPECT

Gold

Titration in acid solution. One mg gold in 20 ml aqueous solution could be determined heterometrically in mineral or acetic acid solution by the titration of gold chloride with rubeanic acid (Table I, Expts. 1-6 and Fig. 1). In each case the end-point of the titration coincided with the first maximum optical density point, which corresponded to the quantitative formation of Au_1R_1 ↓ ↓. After this point a horizontal maximum density line was obtained. The titration lasted 20-30 minutes.

Titrations in alkaline solutions. The titration in strong ammoniacal solution proceeded very quickly (Expt. 13). The first maximum point coincided with the quantitative formation of Au_3R_2 (a brown powder), after which a horizontal maximum density line was obtained. The same ratio was obtained using a solution of Na_2HPO_4 instead of an ammoniacal solution (Expt. 12). The titration time was lengthened considerably in the presence of phosphate. In the presence of ammonia the reaction between gold and rubeanic acid probably occurred with a gold amino complex instead of with a gold chloro complex, as in all other cases.

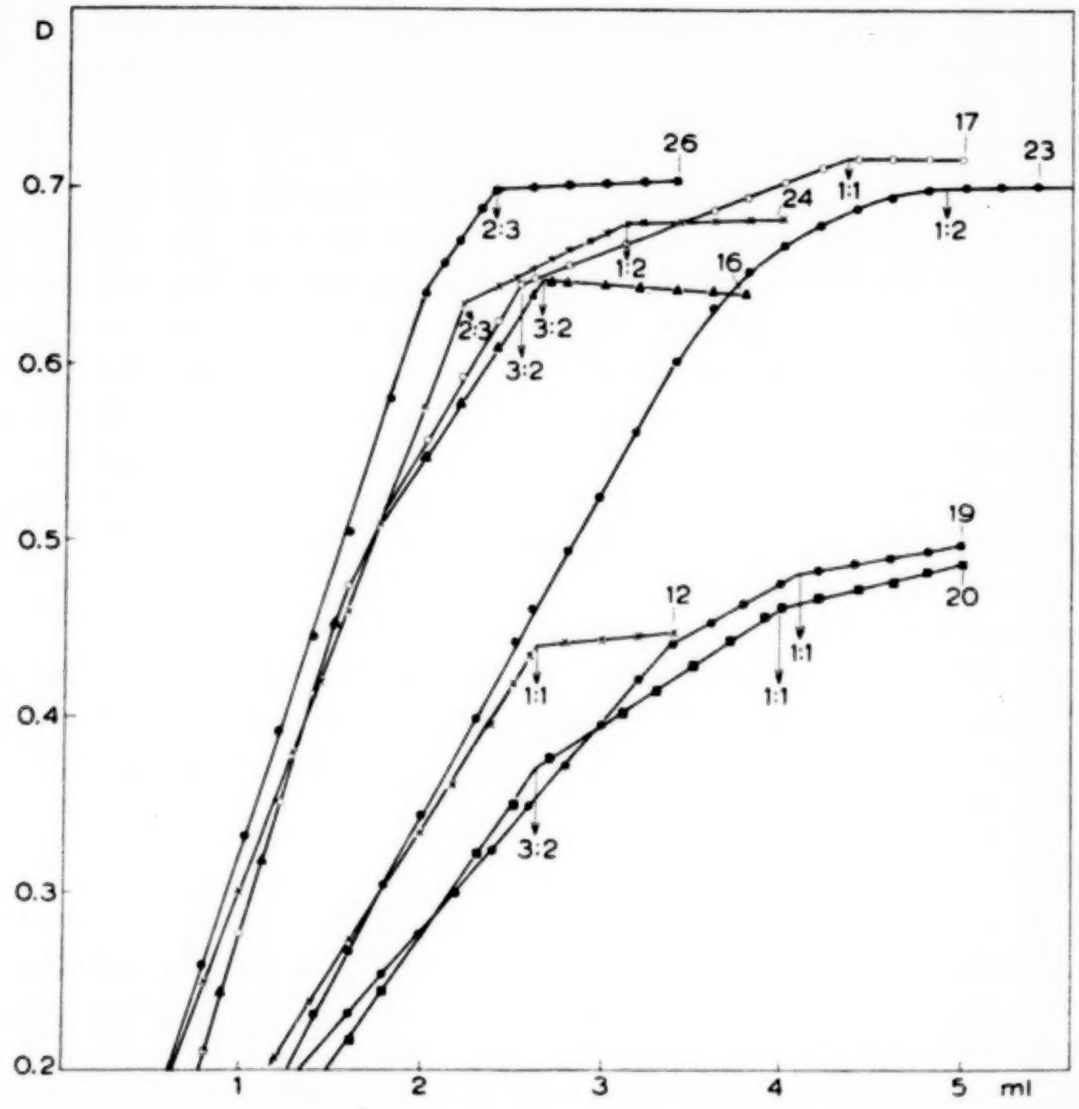


Fig. 2. Titrations of gold chloride or palladium chloride solutions with rubeanic acid.

Palladium

Titrations in acid solution. Table I, Expts. 15-22 give the results of such titrations, which proceeded very quickly. The first maximum density point coincided with the quantitative formation of Pd_3R_2 ↓↓. The error was generally less than 1% (Expts. 15, 16 and 18). After the first maximum point a horizontal line was obtained. On increasing the amount of acid *two* critical points were obtained (Expt. 17): the first at the quantitative formation of Pd_3R_2 and the second at the quantitative formation of Pd_1R_1 ↓↓. The concentration of alkali chloride present was of considerable importance. While the presence of a minimum amount of chloride was essential for the titration of palladium, large amounts of chloride stabilized the chloro-palladium complex (Expt. 19) so that the titration lasted about 90 minutes instead of the usual 15 minutes. The first maximum density point was obtained exactly at the point of the quantitative formation of Pd_1R_1 ↓↓.

When similar titrations were carried out in acetic acid solution (Expt. 20), *two* critical points were obtained: the first corresponded to the quantitative formation of Pd_3R_2 (normal titration time), while the second, which coincided with the first maximum density point, corresponded to the quantitative formation of Pd_1R_1. It is in-

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teresting to compare the two results which were obtained using $PdCl_2$ as titrant (Expts. 21 and 22). In the presence of NH_4Cl the compound Pd_3R_2 was obtained quantitatively (error less than 1%), while in the absence of NH_4Cl, Pd_1R_1 was obtained instead.

Titrations in neutral or alkaline solutions. Table I, Expts. 23-27 and Fig. 2 give the composition and the results of such titrations. In sodium acetate solution, in the absence of alkali chloride, we obtained only the compound Pd_1R_1, but the titration time was very extended (Expt. 23). If NH_4Cl was present in moderate amounts, *two* compounds were obtained successively. The first compound had the composition $Pd_2R_3\downarrow$ and was obtained quantitatively very quickly. On further addition of rubeanic acid the reaction proceeded very slowly, giving the second compound Pd_1R_2 (Expt. 24). When more NH_4Cl was present or when the titration was carried out in the presence of Na_2HPO_4 only *one* compound was obtained, namely Pd_2R_3 but the titration time still remained extended (Expts. 24-27). From these results we may conclude that palladium should be determined in acid solution.

Method. About one mg of palladium (as chloride) in 20 ml solution, containing 1 ml $0.5M$ nitric acid and 1 ml $0.5M$ NH_4Cl or NaCl, is titrated heterometrically with a $\sim 0.002M$ solution of rubeanic acid (alc.). The error is less than 1% and the titration time about 15 minutes.

SOLUBILITY

Some of the precipitates which were obtained before were tested for their solubility in the following organic solvents: chloroform, CS_2, CCl_4, dioxane, acetone, methyl and ethyl alcohol.

Dilute solutions of gold or palladium were titrated according to the experiments of Table I. The suspensions obtained were centrifuged. The aqueous solution was then replaced by ethyl alcohol, and the suspension centrifuged again. Parallel experiments were carried out cooling the reaction vessels in ice. In both cases the solids which were finally obtained were of the same brownish-red colour and showed the same behaviour towards solvents.

Small samples of the solid were tested as to their solubility. The results were as follows. The compounds Au_1R_1 and Au_2R_3 were found to dissolve best in acetone or dioxane, though solution occurred rather slowly. The solutions finally obtained had a brown colour.

The compound Pd_3R_2 was also prepared according to Expt. 15. The reaction occurred almost instantly. The precipitate seemed to be partly soluble in ether and in CS_2. The solution of the compound in acetone had an intense yellow colour.

ELEMENTARY ANALYSIS

Small amounts of the compounds studied were prepared according to the reactions of Table I as described previously. Micro-analyses of the dried compounds were carried out, though unfortunately not more than a few milligrams were available for each analysis. More satisfactory results were obtained with the gold than with the palladium compounds. In each case the percentage of nitrogen and carbon in the compound were determined. We present here some of the results obtained.

Au_1R_1 was prepared according to Expt. 3, Table I, and analyzed:

	Calculated	*Found*
N:	8.83%	7.21%
C:	7.56%	7.03%

Au_2R_3 was prepared according to Expt. 7, Table I, and analyzed:

	Calculated	*Found*
N:	11.1 %	9.4 %
C:	9.54%	9.51%

Au_3R_2 was prepared according to Expt. 13, Table I. The amounts of both nitrogen and carbon that were found were very low. The compound may have decomposed during its preparation.

Pd_2R_3 was prepared according to Expt. 27, Table I, and analyzed:

	Calculated	*Found*
N:	14.61%	9.2%
C:	12.56%	12.4%

DISCUSSION

It is remarkable that the insoluble compounds obtained with auric gold and with palladium have similar stoichiometric composition, although the pH's at which compounds having similar compositions are obtained differed for the two metals. However, since the valencies of the metals are different, the compounds obtained may still have different composition.

Thus we obtain at pH 1-3 the compound Au_1R_1, while the corresponding compound with palladium consists of Pd_3R_2. Also, the gold compound which was obtained at pH ∼ 5 and has the composition Au_2R_2 may correspond to the palladium compound Pd_1R_1 which was obtained at pH ∼ 3. Furthermore, the palladium compound Pd_3R_2 may easily be transformed by further addition of rubeanic acid into Pd_1R_1, while the palladium compound Pd_2R_3, obtained at pH 7-8, may similarly be transformed into Pd_1R_2. It therefore seems probable that some similarity in the structures must exist. The probability that a particular palladium compound was formed depended, amongst other factors, on the amount of chloride present in solution. On the other hand, no transformations were observed in the case of gold, the composition of the compounds obtained depending only on the pH of the solution.

We shall now try to present structural formulae for the above compounds on the basis of their behaviour.

The compound Pd_1R_1 may be represented schematically by

$$\left[\mathrm{Pd} \overset{\leftarrow}{\underset{\leftarrow}{=}} \mathrm{R}\right]^\circ \qquad (1)$$

$$\begin{tikzcd} & \mathrm{Pd} \arrow[dr] & \\ \mathrm{R} \arrow[ur] \arrow[dr] & & \mathrm{R} \arrow[dl] \\ & \mathrm{Pd} & \end{tikzcd} \qquad (2)$$

or

$$\begin{tikzcd} \mathrm{R} \arrow[r] \arrow[d] & \mathrm{Pd} & \mathrm{R} \arrow[l] \arrow[d] \\ \mathrm{Pd} & \mathrm{R} \arrow[l] \arrow[r] & \mathrm{Pd} \end{tikzcd} \qquad (3)$$

Pd_1R_1 always appears as the final (= ↓↓) compound.

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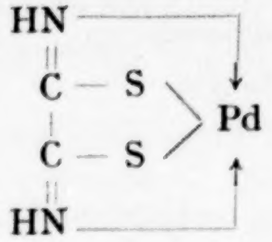
The monomer may have the following structure:

(4)



More complicated is the structure of the polymer. The latter would perhaps sustain less stress.

Pd_1R_2 may be represented schematically by:

$$\left[R \stackrel{-}{\rightarrow} Pd \stackrel{-}{\leftarrow} R\right]^\circ \quad \text{or} \quad \left[R = Pd \rightleftarrows R\right]^\circ$$

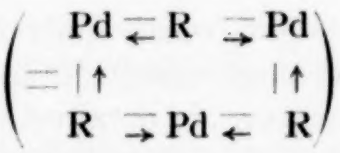
(5) (6)

Pd_3R_2 was obtained at pH 1-3 and was sometimes transformed into Pd_1R_1. Schematically this transformation may be represented as follows:

(7)

$$\left[\begin{matrix}\text{Cl.}\\ \text{aq.}\end{matrix}\ Pd \stackrel{-}{\leftarrow} R \stackrel{-}{\rightarrow} Pd \stackrel{-}{\leftarrow} R \stackrel{-}{\rightarrow} Pd\ \begin{matrix}\text{.Cl}\\ \text{.aq}\end{matrix}\right]^\circ \xrightarrow{+R} \left[PdR\right]_3$$

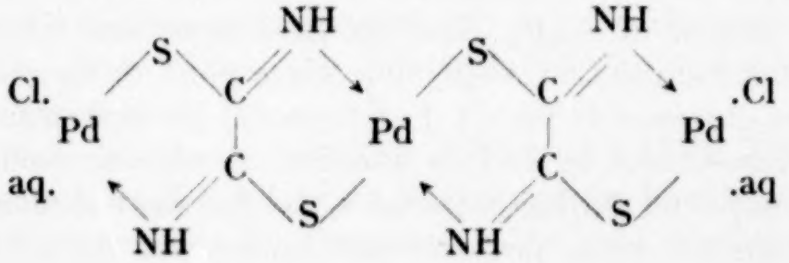
(8)



$$\left(\begin{matrix} & Pd \stackrel{-}{\leftarrow} R \stackrel{-}{\rightarrow} Pd \\ = & | \uparrow \qquad\quad | \uparrow \\ & R \stackrel{-}{\rightarrow} Pd \stackrel{-}{\leftarrow} R \end{matrix}\right)$$

The structure of Pd_3R_2 may be represented as follows:

(9)



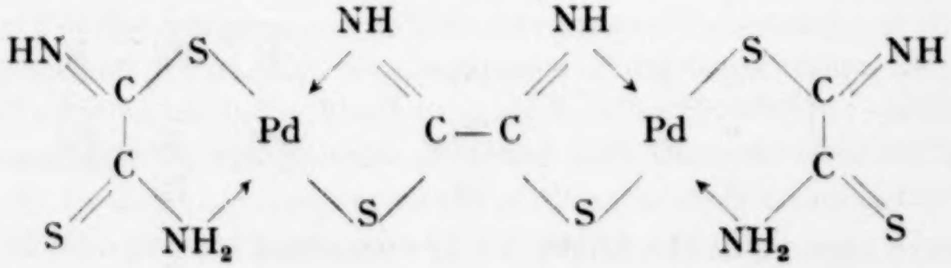
Pd_2R_3 was obtained at pH 7-8 and was sometimes transformed into PdR_2. Schematically this transformation may be represented as follows:

(10)

$$R \stackrel{-}{\rightarrow} Pd \stackrel{-}{\leftarrow} R \stackrel{-}{\rightarrow} Pd \stackrel{-}{\leftarrow} R \xrightarrow{+R} 2\left[R \stackrel{-}{\rightarrow} Pd \stackrel{-}{\leftarrow} R\right]^\circ$$

Pd_2R_3 most probably has the following structure:

(11)



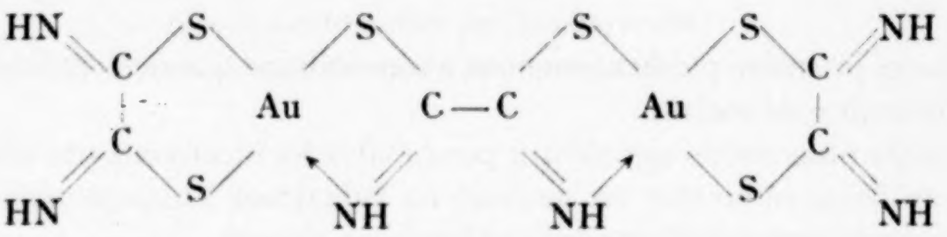
With regard to the structure of the gold compounds, since they are not transformed one into the other, it is less easy to ascribe definite structures to them. Thus, we are not sure that the compound Au_3R_2 is really a rubeanate and not a sulfide.

The compound Au_2R_3, which was obtained at pH 5-7, may be represented schematically by:

$$\left[R = Au \leftarrows R \rightarrows Au = R\right]^\circ \qquad (12)$$

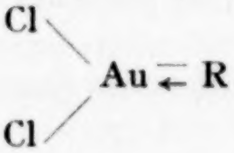
It most probably has the following structure:

(13)



No definite structure can be given to the compound Au_1R_1 which was obtained at pH 1-3. It can perhaps be represented by:

(14)



$$\begin{matrix} Cl \\ & Au \leftarrows R \\ Cl \end{matrix}$$

SUMMARY

Both palladium and gold(III) formed three insoluble compounds with rubeanic acid: Me_1R_1, Me_2R_3 and Me_3R_2. The pH at which the compounds were formed was studied. Structural formulae for the compounds are presented. Methods are described for the determination of 1 mg metal in 20 ml solution.

RÉSUMÉ

Le palladium ainsi que l'or(III) donnent trois dérivés insolubles avec l'acide rubéanique: Me_1R_1, Me_2R_3 et Me_3R_2. Le pH auquel ces trois dérivés se forment a été étudié. Des formules structurelles sont présentées pour ces dérivés.

Des méthodes sont données pour la détermination de 1 mg de métal dans 20 ml de solution.

ZUSAMMENFASSUNG

Sowohl Palladium als auch Gold(III) geben drei unlösliche Verbindungen mit Rubeansäure: Me_1R_1, Me_2R_3 und Me_3R_2. Das pH bei welchem die Verbindungen gebildet werden, wurde studiert. Strukturformeln für die Verbindungen wurden präsentiert.

Methoden wurden angegeben für die Bestimmung von 1 mg Metall in 20 ml Lösung.

REFERENCES

[1] F. Feigl, *Chemistry of specific, selective and sensitive reactions*, Academic Press, Inc., 1949.

[2] See literature on heterometry 1953-1956 in *Anal. Chim. Acta*, 16 (1957) 75;
M. Bobtelsky and R. Rafailoff, *ibid.*, 16 (1957) 321, 488; 17 (1957) 267, 308.
M. Bobtelsky and J. Eisenstadter, *ibid.*, 16 (1957) 479; 17 (1957) 503.

[3] M. Bobtelsky, *ibid.*, 13 (1955) 172.

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DOSAGE COLORIMÉTRIQUE DU FER DANS L'ACIDE PHOSPHORIQUE ET SES SELS

par

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Dans notre première publication nous avons indiqué que nous réduisons Fe^{+3} en Fe^{+2} par l'hydrosulfite de sodium[1].

Par la suite nous avons signalé que pour éviter les inconvénients inhérents à un trop large excès de ce réducteur on pouvait lui substituer l'hypophosphite de sodium, à condition de consentir à effectuer la réduction à chaud[2].

Bien qu'en présence d'acide phosphorique et d'hydroxydes aliphatiques, certains auteurs réduisent Fe^{+3} par l'hydroxylamine, nous avons constaté que leur présence inhibait la réduction dans une mesure telle que la teinte évoluait avec le temps, et n'atteignait son maximum qu'après plusieurs heures et cela tant avec le dipyridyle qu'avec l'*ortho*-phénanthroline.

En opérant sur une solution renfermant dans 100 ml:

Acide phosphorique de densité $d = 1.17$	2 ml
Acide citrique	1 g
Fe^{+3}	200 γ

nous avons suivi au spectrophotomètre la variation de la densité optique en fonction du temps, selon que la réduction était effectuée par 1 g de chlorhydrate d'hydroxylamine ou par 0.05 g d'hydrosulfite de sodium.

La courbe qui représente cette variation indique qu'avec l'hydrosulfite la teinte atteint son maximum en une heure.

Ce temps est porté à 20 heures en présence d'hydroxylamine.

Le but de nos recherches a été:

1°. Améliorer le mode opératoire de la réduction par l'hydrosulfite.

2°. Eviter la précipitation de soufre qui se produit chaque fois qu'il y a un trop large excès de ce réactif.

Nous avons pensé que la destruction de l'hydrosulfite avec formation de soufre pouvait être la conséquence d'un pH trop bas.

En opérant sur la solution dont la composition a été indiquée plus haut, nous avons tamponné le milieu pour obtenir des pH de: 3, 4, 5, 6, 7; nous avons ensuite réduit Fe^{+3} par 0.5 g d'hydrosulfite, soit par 10 fois la quantité nécessaire pour avoir une précipitation de soufre.

Nos constatations sont les suivantes:

à pH = 3, il y a précipitation immédiate et abondante de soufre;

à pH = 4, la précipitation de soufre est très faible et ne se produit qu'au bout de quelques heures.

Entre pH = 5 à 7, il n'y a pas de précipitation de soufre, et la solution reste limpide même après plusieurs jours.

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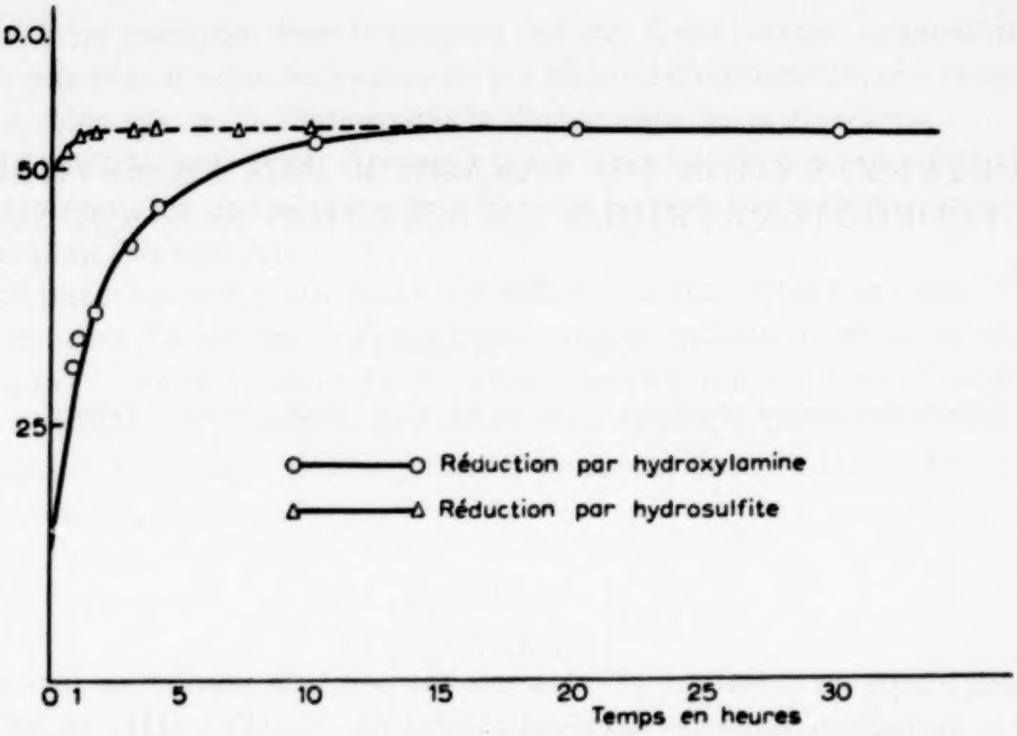

Fig. 1. Variation de la densité optique en fonction du temps pour $FeCl_3$ réduit par l'hydroxylamine ou par l'hydrosulfite de sodium en présence d'acide phosphorique et d'acide citrique. Dans 100 ml: acide citrique, 1 g; acide phosphorique ($d = 1.17$), 2 ml; Fe^{+3}, 200 γ, pH = 5.

En ce qui concerne la stabilité de la teinte nous avons observé qu'elle atteignait son maximum en 1 heure jusqu'à pH = 6, puis qu'au pH = 7, elle ne se développait que plus lentement.

En conclusion: lorsqu'il s'agit de doser colorimétriquement le fer en présence d'acide phosphorique et d'hydroxydes aliphatiques, il convient de réduire le fer par l'hydrosulfite et non par l'hydroxylamine.

En opérant sur des solutions de pH compris entre 5 et 6, un excès d'hydrosulfite n'est pas gênant.

Nous avons vérifié qu'à ces pH le calcium et l'aluminium ne précipitaient pas en présence de 1 g d'acide citrique pour 100 ml de solution.

RÉSUMÉ

En présence d'acide phosphorique et d'hydroxydes aliphatiques, la réduction du fer trivalent par l'hydroxylamine est très lente. Pour le dosage colorimétrique par le dipyridyle et l'*ortho*-phénanthroline, il convient d'utiliser l'hydrosulfite et d'opérer à un pH compris entre 5 et 6 pour éviter la précipitation de soufre consécutive à un excès de ce réducteur. Au-dessus d'un pH = 6, la teinte se développe plus lentement.

SUMMARY

In the presence of phosphoric acid and aliphatic hydroxides, reduction of trivalent iron by hydroxylamine is very slow. For colorimetric estimation with dipyridyl and *ortho*-phenanthroline, it is convenient to use hydrosulphite and to work at a pH of 5-6 in order to avoid the precipitation of sulphur resulting from an excess of this reducing agent. At pH higher than 6 the colour develops more slowly.

ZUSAMMENFASSUNG

In Gegenwart von Phosphorsäure und aliphatischen Hydroxyden verläuft die Reduktion des dreiwertigen Eisens mittels Hydroxylamin sehr langsam. Zur kolorimetrischen Bestimmung mit Dipyridyl und *ortho*-Phenantrolin empfiehlt es sich, Hydrosulfit zu verwenden und bei einem pH von 5 bis 6 zu arbeiten, um die Fällung von Schwefel bei Anwesenheit eines Überschusses an Reduktionsmittel zu vermeiden. Bei einem höheren pH als 6 entwickelt sich die Farbe langsamer.

BIBLIOGRAPHIE

[1] M. Grat-Cabanac, *Anal. Chim. Acta*, 5 (1951) 116.
[2] M. Grat-Cabanac, *Anal. Chim. Acta*, 16 (1957) 150.

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LA DÉTERMINATION DU VANADIUM PAR LA MÉTHODE SPECTROPHOTOMÉTRIQUE EN SOLUTION NON-AQUEUSE

par

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Depuis longtemps on a élaboré et on a mis au point de nombreux procédés pour déterminer le vanadium, dans ses degrés d'oxydation (V), (IV), (III), en utilisant les méthodes colorimétrique et spectrophotométrique.

Ces méthodes se fondent sur:

(a) *L'emploi de réactifs inorganiques* pour la formation de composés fortement colorés. L'eau oxygénée produit des peroxy-composés de couleur rouge orange[1]; les thiocyanates donnent des complexes thiocyaniques avec le vanadium(III) qui présentent un maximum d'absorption à 395 mμ[2]; Na_2S en solution alcaline forme des thiovanadates de couleur rouge[3]; les ferro- et ferricyanures forment des solutions colloïdales fortement colorées de ferro- et de ferricyanures ~~de~~ vanadyle[4]; les réactifs réducteurs tels que SO_2 permettent de réduire les vanadates en sels de vanadyle bleus[5].

(b) *L'emploi de réactifs organiques* pour la formation de composés colorés solubles même dans les dissolvants organiques. Ainsi, avec le cupferron[6] on obtient avec vanadium(V) un composé soluble dans l'acétone avec coloration verte; avec la 8-hydroxyquinoléine[7] en solution chloroformique, on a une forte coloration qui permet de doser 1-50 γ de vanadium; avec l'acide benzohydroxamique[8] on forme avec le vanadium(V) en solution fortement acide des complexes de couleur bleue, de couleur rouge en solution faiblement acide ou alcaline; avec l'acide salicyl-hydroxamique[9] on obtient une coloration bleu-violette ayant un maximum d'absorption entre 470 et 500 mμ à pH 3.02-3.80. On a aussi proposé d'employer l'*o*-dianisidine[10], la formaldoxime[11], la pyrocatéchine[12].

(c) *L'utilisation des propriétés oxydantes du vanadium (V)* sur les substances inorganiques et organiques. Ainsi l'acide vanadique est capable d'oxyder en milieu acide l'ion I^- en iode. Ceci peut être dosé colorimétriquement[13]. Les sels de vanadyle réduisent les sels ferriques en sels ferreux qu'on dose spectrophotométriquement avec la diméthylglyoxime[14]. La diphénylbenzidine est oxydée par vanadium(V) en solution 10N de H_3PO_4 avec apparition d'une forte coloration bleue[15].

On ne peut pas dire toutefois qu'on a résolu d'une manière satisfaisante le problème de la détermination du vanadium à échelle microchimique, car les méthodes employées à présent se fondent sur des phénomènes, provoquées indirectement par la présence du vanadium, auxquels d'autres éléments peuvent cependant participer obtenant des résultats identiques, ou sur des réactions communes à plusieurs éléments. Bien nombreuses sont en effet les interférences que plusieurs auteurs citent au sujet de leurs

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méthodes: c'est pourquoi dans la plupart des cas, il est presque impossible que d'employer tel procédé ou tel autre à cause de la difficulté d'éliminer les réactions communes à d'autres éléments ou de l'impossibilité d'accomplir les séparations.

Il nous a pourtant paru bon de retenir toute tentative de mise au point d'un procédé de dosage présentant une bonne sensibilité, un nombre d'interférences petit, et étant spécifique pour le vanadium.

Dans ce but nous avons fait usage des recherches conduites par COZZI ET CECCONI[16] sur les composés d'addition de l'oxychlorure de vanadium(V) et du tétrachlorure de vanadium avec les aldéhydes et d'autres composés organiques dans un milieu anhydre.

Parmi les différents composés que nous avons étudié, le composé obtenu par $VOCl_3$ avec l'aldéhyde salicylique semble posséder un certain intérêt dans le but d'éventuelles applications analytiques.

$$\left[\begin{matrix} C_6H_4\cdot CHO\cdot O \\ C_6H_4\cdot CHO\cdot OH \end{matrix}\right] VOCl_2$$

est peu soluble dans les solvants organiques, a une forte coloration bleue et une stabilité, même à l'égard de l'humidité, bien supérieure à celle présentée par divers produits d'addition entre $VOCl_3$, les aldéhydes et les autres composés, y compris le dioxane.

En effet, si à une solution de $VOCl_3$, dans CCl_4 contenant du dioxane qui présente une vive couleur rouge, on ajoute de l'aldéhyde salicylique, la couleur de la solution vire du rouge au violet ou au bleu selon que l'aldéhyde salicylique qu'on a introduit est en défaut ou en excès par rapport au dioxane.

De recherches ultérieures, il résulte que — outre l'aldéhyde salicylique — plusieurs autres composés ont un comportement analogue envers le $VOCl_3$. Comme il ressort du Tableau I, l'agent réactif fondamental est l'hydroxyle énolique. Il agit favorablement lorsqu'il est uni au groupe benzénique et la coloration qu'il produit est conditionnée par la présence en *ortho* d'un groupe carbonyle.

On peut pourtant employer avantageusement — outre l'aldéhyde salicylique — l'acide salicylique, le salicylate de méthyle, d'éthyle, etc. Au point de vue de l'application pratique il n'est pas possible d'effectuer la transformation du vanadium en $VOCl_3$ et d'accomplir tout de suite la synthèse des composés susdits.

Évidemment il faut simplifier le procédé pour rendre possible la préparation des composés susdits en une seule opération, en phase liquide, à partir des solutions aqueuses.

Lorsqu'on traite des solutions aqueuses qui contiennent un vanadate alcalin avec HCl gazeux, on voit apparaître une remarquable coloration rouge foncé lorsque la concentration de HCl dépasse $9M$. La couleur qui ne peut pas être confondue avec celle de l'acide vanadique est identique à celle qu'on obtient en dissolvant $VOCl_3$ dans HCl concentré.

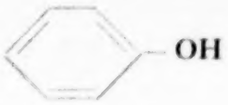
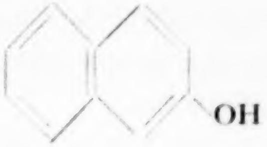
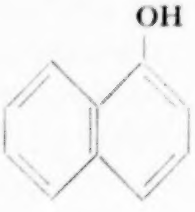
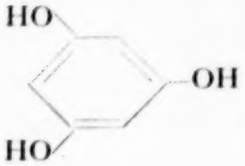
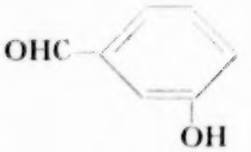
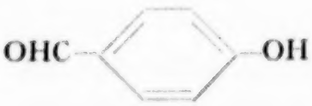
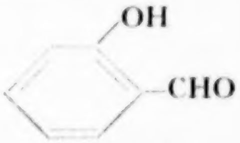
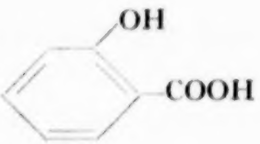
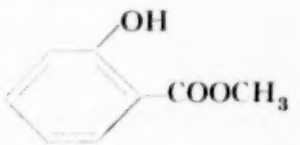
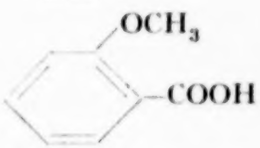
A la suite des recherches faites en même temps par COZZI, on doit attribuer au composé fortement coloré en rouge foncé une structure analogue à celle du $VOCl_3$ avec le dioxane: la seule différence est que, dans ce cas, l'eau est l'agent solvatant.

On peut schématiser les réactions de la manière suivante:

$$VO_3^- + H_3^+O \rightleftarrows HVO_3 + H_2O \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$HVO_3 + 3\ HCl \rightleftarrows VOCl_3.2H_2O\ \text{(rouge)} \quad \ldots\ldots\ldots \quad (2)$$

TABLEAU I

Réactifs	*Réaction*	*Réactifs*	*Réaction*
	coloration bleue faible		pas de coloration
	pas de coloration		coloration faible
	pas de coloration	$CH_3·CHOH·COOH$	pas de coloration
	pas de coloration	$CHOH·COOH$ $CHOH·COOH$	pas de coloration
$CH_3·CO·CH_2·COO·C_2H_5$	coloration grise		coloration violette bleue
	coloration bleue violette		coloration violette
			pas de coloration

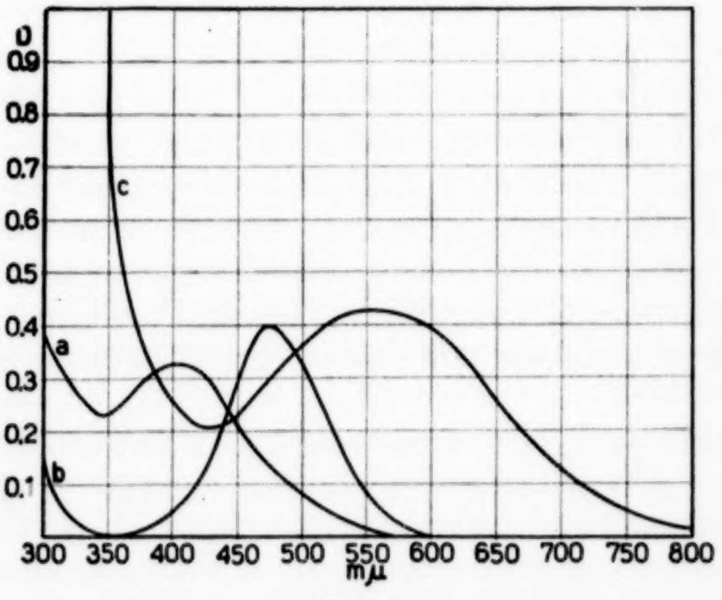


Fig. 1.

(a) Courbe d'absorption de solutions de vanadium(V) dans le dioxane *N* en HCl.
(b) Courbe d'absorption de solutions de vanadium(V) dans l'anhydride acétique *N* en HCl.
(c) Courbe d'absorption de solutions de vanadium(V) dans l'anhydride acétique *N* en HCl contenant 20% de salicylate de méthyle.

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Ce procédé donne la possibilité d'obtenir les conditions nécessaires à la formation des composés du vanadium avec l'aldéhyde salicylique ou avec des composés équivalents, même si on ne peut disposer que de solutions aqueuses de vanadates alcalins au lieu de $VOCl_3$ anhydre dissous dans des solvants organiques. En effet, si on ajoute l'aldéhyde salicylique à de solutions de $VOCl_3.2H_2O$ dans HCl concentré, on voit changer la couleur rouge foncée en bleu vif, de la même façon qu'on peut le voir avec les solutions du composé $VOCl_3.O(CH_2CH_2)_2O$ dans le mélange CCl_4 et dioxane.

L'eau, comme solvant, n'empêche pas la formation des composés colorés du vanadium, à condition qu'elle présente une activité en ions hydrogène au moins supérieure à 70: toutefois elle ne permet pas la conservation, particulièrement si on fait des solutions très diluées de vanadium.

Si on remplace une grande partie de l'eau par du dioxane anhydre contenant HCl gazeux dissous, on peut dire que les résultats sont meilleurs, mais qu'ils ne sont pas encore satisfaisants (Fig. 1a et 2a).

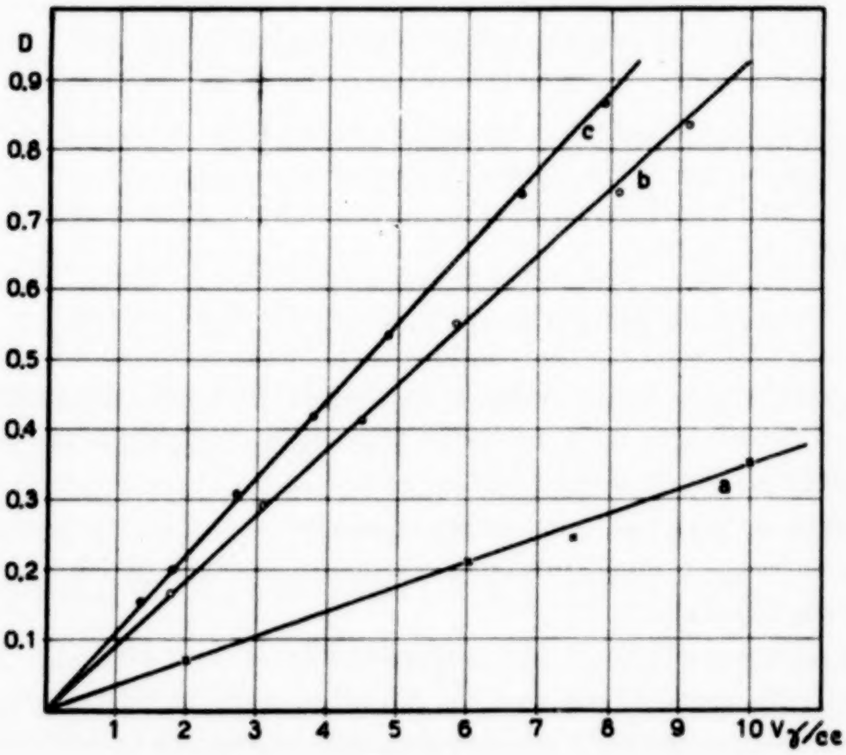


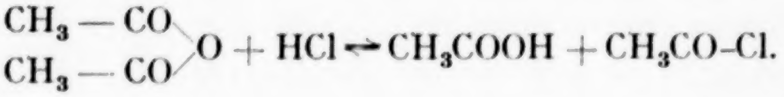
Fig. 2.

(a) Courbe d'étalonnage de solutions de vanadium(V) dans le dioxane anhydre *N* en HCl à 410 mμ.
(b) Courbe d'étalonnage de solutions de vanadium(V) dans l'anhydride acétique *N* en HCl à 475 mμ.
(c) Courbe d'étalonnage de solutions de vanadium(V) dans l'anhydride acétique *N* en HCl contenant 20% de salicylate de méthyle à 565 mμ.

Pour obtenir la stabilité absolue des produits de la réaction il faut éliminer toute l'eau de la solution, même celle qu'on doit inévitablement employer comme dissolvant du vanadate alcalin.

Les recherches ont été orientées sur l'emploi de matières très déshydratantes. Après avoir écarté l'acide sulfurique concentré, l'anhydride phosphorique et le chlorure de phosphore parce qu'ils ne convenaient pas ou parce que leur emploi n'était pas facile, nous avons pensé à utiliser l'anhydride acétique.

En effet, en dissolvant dans celui-ci HCl gazeux (HCl est, pour l'accomplissement de la réaction (2), indispensable) on obtient un fort échauffement, dû surtout à la formation de chlorure d'acétyle:



$$\begin{matrix} CH_3-CO \\ CH_3-CO \end{matrix}\Big\rangle O + HCl \rightarrow CH_3COOH + CH_3CO\text{-}Cl \quad \ldots\ldots\ldots \quad (3)$$

L'opération doit être prolongée jusqu'à ce que l'anhydride acétique soit molaire en chlore total.

Une telle solution, qui a une odeur piquante et irritante, se prête très bien à remplacer l'acide chlorhydrique concentré dans la préparation des solutions de vanadate sodique et à fournir les réactifs nécessaires à la formation d'une couleur rouge très forte et stable, à cause de l'absence d'eau.

L'anhydride acétique possède avec le chlorure d'acétyle non seulement des propriétés déshydratantes, mais aussi des propriétés liantes très semblables à celles du dioxane, et c'est pour cela qu'avec $VOCl_3$ elle donne naissance à un composé d'addition qui présente un maximum d'absorption à 475 mμ (Fig. 1b),

Au contraire du procédé utilisant des solutions obtenues avec HCl concentré, où la coloration apparaît tout de suite au moment du mélange, dans ce cas, en ajoutant la solution aqueuse de vanadate à l'anhydride acétique et au chlorure d'acétyle, on n'obtient la coloration qu'après quelques minutes.

On doit rechercher l'explication de ce fait dans la lenteur de la réaction d'hydratation du chlorure d'acétyle:

$$CH_3{-}CO{-}Cl + H_2O \rightarrow CH_3COOH + HCl \quad \ldots\ldots\ldots \quad (4)$$

et par conséquent dans la petite vitesse avec laquelle l'eau disparaît du système.

Des mesures de conductivité effectuées dans ce but expliquent clairement ce phénomène: la couleur apparaît seulement après que la résistance spécifique de la solution a dépassé la valeur de $5 \cdot 10^4\ \Omega$, c'est à dire après que l'eau qui se trouvait au commencement dans la mélange a pratiquement disparu à la suite de l'hydrolyse du chlorure d'acétyle (voir réaction (4)).

On a choisi la solution d'anhydride acétique molaire dans HCl afin d'avoir un moyen déshydratant ni trop lent ni trop rapide. En effet, avec la même proportion d'eau on aurait pu obtenir beaucoup plus rapidement une résistance spécifique élevée en utilisant des solutions concentrées, mais il se produit alors un sensible réchauffement de la solution.

Il a été possible de remarquer expérimentalement qu'on obtient les meilleurs résultats en opérant à la température ambiante et en éliminant toute cause de réchauffement (Fig. 2b).

Si, aux solutions dans l'anhydride acétique, on ajoute de l'aldéhyde salicylique ou de l'acide salicylique, on voit tout de suite virer la couleur rouge au violet et au bleu, qui, dans ces conditions d'absence d'humidité, se révèle stable dans le temps.

Si on emploie le salicylate de méthyle qui présente une stabilité plus grande à l'égard de l'aldéhyde salicylique, on peut considérer les résultats obtenu comme vraiment satisfaisants.

On doit opérer de la façon suivante:

On fait évaporer à sec à 100° une fraction de la solution qui contient le vanadium. On reprend le résidu avec 0.2 ml de solution normale de HCl dans de l'eau à 2% de

H_2O_2, de façon à transformer le vanadium à l'état de peroxycomposé; puis on ajoute, tout en refroidissant et en agitant, 5 ml de la solution suivante:

$$\left.\begin{array}{ll}\text{anhydride acétique } M \text{ en HCl gazeux} & 40 \text{ ml}\\ \text{acide acétique glacial} & 40 \text{ ml}\\ \text{salicylate de méthyle} & 20 \text{ ml}\end{array}\right\}\ \text{(A)}$$

Peu de temps après paraît une coloration violette bleue dont la courbe d'absorption de la lumière visible est reportée à la Fig. 1c. La Fig. 2c représente la courbe d'étalonnage pour les mesures effectuées à 565 mμ avec cuvette de 1 cm.

La méthode se révèle hautement spécifique et bien sensible.

Le fer(III) lui-même s'il est présent en poids 2000 fois supérieur ne gène pas la détermination, même si la couleur de la solution paraît verdâtre.

A la longueur d'onde 565 mμ, le fer dans ces conditions ne produit aucune absorption.

Le cuivre, le nickel, le cadmium, l'uranium, le chrome n'interfèrent pas s'ils se trouvent en petites quantités (jusqu'à 10 fois en poids); de fortes quantités provoquent un précipité. Par centrifugation on sépare le précipité de la solution, qu'on va mesurer sans interférences ni troubles.

Le cobalt, le molybdène, le tungstène ne doivent pas être présents car ils présentent respectivement une couleur verte bleue, bleue, jaune rouge, avec absorption sensible à 565 mμ.

L'aluminium en fortes quantités (supérieures à 100 fois) catalyse fortement le processus de déshydratation des solutions avec développement de chaleur. S'il est présent, il vaut mieux employer la solution suivante au lieu de la solution A: anhydride acétique 40 ml, acide acétique glacial 40 ml, salicylate de méthyle 20 ml.

Les autres éléments ne gênent pas.

REMERCIEMENT

Ce travail a été effectué avec la contribution du C.N.R.

RÉSUMÉ

Quand on mélange de petits volumes de solution aqueuse de vanadium contenant de l'eau oxygénée et acidifiée par HCl, à du dioxane anhydre contenant de l'acide chlorhydrique gazeux dissous en concentration molaire, il apparaît une coloration intense jaune rouge avec 5 μg/ml de vanadium seulement.

Si à la solution ainsi obtenue on additionne une goutte d'aldéhyde salicylique, la coloration vire au bleu-violet qui présente un maximum d'absorption à 565 mμ, clairement visible même avec 1 μg/ml de vanadium.

La réaction tant en donnant une méthode sensible pour la recherche du vanadium, ne se prête pas à la mesure quantitative de celui-ci car la petite quantité d'eau introduite sous forme de solution de vanadium agit hydrolytiquement sur les composés colorés, en déterminant leur dégradation.

On obtient des resultats très bons en reprenant le résidu sec (à 100°C) de la solution prise en examen avec 0.2 ml de HCl N dans de l'eau à 2% de H_2O_2, et après avec 5 ml de solution composée de 40% d'anhydride acétique N en HCl gazeux, de 40% d'acide acétique glacial et de 20% de salicylate de méthyle.

La méthode nous permet de déterminer jusqu'à 1 μg de vanadium.

Co, Mo, W donnent des interférences. Les autres éléments ne gênent pas.

SUMMARY

On mixing small quantities of an aqueous solution of vanadium, containing hydrogen peroxide and acidified with HCl, with anhydrous dioxan containing gaseous hydrogen chloride in molar concentration, an intense red-yellow colour appears in the presence of as little as 5 μg/ml vanadium.

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If a drop of salicylic aldehyde is added to the solution thus obtained, the colour changes to violet-blue, which shows an absorption maximum at 565 mμ, clearly visible even with 1 μg/ml vanadium.

This reaction, though a sensitive method for the detection of vanadium, is not suitable for quantitative measurement of this substance because the small quantity of water introduced in the form of the vanadium solution hydrolyses the coloured compounds.

Very good results can be obtained by dissolving the dry residue (at 100°C) of the solution under examination in 0.2 ml of *N* HCl in 2% aqueous H_2O_2 solution, and then in 5 ml of a solution made up of 40% acetic anhydride containing gaseous HCl (1*N*), 40% glacial acetic acid, and 20% methyl salicylate.

By this method as little as 1 μg of vanadium can be determined.

Co, Mo, and W, interfere; the other elements do not.

ZUSAMMENFASSUNG

Mischt man kleine Volumina einer wässrigen Vanadinlösung die Wasserstoffperoxyd enthält und mit Salzsäure angesäuert ist, mit wasserfreiem Dioxan welches gasförmige Salzsäure in molarer Konzentration enthält, so entsteht eine intensive rot-gelbe Färbung, wenn nur 5 μg/ml Vanadin gegenwärtig sind.

Fügt man zu der so erhaltenen Lösung einen Tropfen Salicylaldehyd so schlägt die Farbe in violett-blau um und zeigt ein Absorptionsmaximum bei 565 mμ, das selbst mit 1 μg/ml Vanadin deutlich sichtbar ist.

Diese Reaktion ermöglicht einen empfindlichen Nachweis des Vanadins, eignet sich aber nicht für dessen quantitative Bestimmung da die kleine in der Vanadinlösung enthaltene Wassermenge die gefärbten Verbindungen hydrolysiert.

Sehr gute Ergebnisse werden erhalten wenn man den Rückstand (bei 100°C) der zu prüfenden Lösung mit 0.2 ml *N* HCl in 2%iger wässriger H_2O_2-Lösung und dann mit 5 ml einer Lösung versetzt die sich 40% einer normalen HCl-Lösung in Essigsäureanhydrid, 40% Eisessig und 20% Methylsalicylat zusammensetzt.

Mit Hilfe der beschriebenen Methode kann man bis zu 1 μg Vanadin bestimmen. Co, Mo, und W stören, die anderen Elemente stören nicht.

BIBLIOGRAPHIE

[1] M. K. Berezova, *Gigiena i Sanit.*, 7 (1951) 30.
H. C. Davis et A. Bacon, *Selected Govt. Research Repts. (G. Brit.)*, 3 (1951) 295.
[2] C. E. Crouthamel, *Anal. Chem.*, 27 (1955) 507.
[3] F. D. Snell et C. T. Snell, *Colorimetric Methods of Analysis*, Vol. II, 2nd Ed., D. Van Nostrand Co., New York, 1949, p. 520.
[4] R. V. Vorontsov, *Zavodskaia Lab.*, 13 (1947) 1155.
[5] R. Santini, *Anal. Chim. Acta*, 6 (1952) 368.
[6] H. H. Willard, E. L. Martin et R. Feltham, *Anal. Chem.*, 25 (1953) 1863.
[7] N. A. Talvitie, *Anal. Chem.*, 25 (1953) 604.
R. Montequi et M. Gallego, *Anales soc. españ. fís. y quím.*, 32 (1934) 134.
J. M. Bach et R. A. Trelles, *Anales asoc. quím. arg.*, 28 (1940) 111.
[8] A. K. Das Gupta, *J. Sci. Ind. Research (India)*, 11 B (1952) 268.
[9] A. S. Baduri, *Sci. and Culture (India)*, 18 (1952) 97.
[10] F. Buscarons Ubeda, *Anales fís. y quím. (Madrid)*, 41 (1945) 249.
[11] Motoharu Tanaka, *Mikrochim. Acta*, 42 (1954) 701.
[12] V. Patrowski, *Chem. listy*, 49 (1955) 854.
[13] V. Ramanjaneyulu, *Proc. Nat. Inst. Sci. India*, 11 (1945) 331.
[14] N. Oi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 75 (1954) 841.
[15] V. L. Meaurio, *Ann. chim. anal.*, 23 (1918) 47.
[16] D. Cozzi et S. Cecconi, *Ricerca. sci.*, 23 (1953) 609.

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A FLAME SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF NICKEL AND BORON IN PLATING SOLUTIONS

by

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INTRODUCTION

The quantitative determination of nickel and boron in nickel plating solutions is of importance to electroplating operations, and a rapid and accurate method for the routine determination of these elements is desirable. The classical gravimetric procedure[1] in which the nickel is precipitated as nickel dimethylglyoxime, dried at 120°C and weighed, does not meet the first of these conditions. DEAN AND THOMPSON[2] have made a study of the flame photometric determination of boron in 1 to 1 methanol–water solution using the boron oxide band system; therefore, the application of this method to the determination of both boron and nickel was examined.

The flame spectrum of nickel as recorded by WATANABE AND KENDALL[3] showed several lines which would be usable as analytical lines: one at 341.5 mμ, one at 351.5 mμ, and another at 352.5 mμ. Of these lines the 352.5 mμ line was chosen because of its increased sensitivity. The boron oxide band system maximum at 518 mμ was used for the measurement of the boron emission intensities.

EXPERIMENTAL

Apparatus

A Beckman Model DU spectrophotometer with Model 9220 flame attachment and Model 4300 photomultiplier unit was used. The excitation source used was a Model 4020 oxygen–hydrogen atomizer-burner.

Reagents

A stock solution containing 65 mg of nickel per ml was prepared by dissolving 11.7 g of reagent grade nickel chloride hexahydrate and 16.1 g of nickel sulfate hexahydrate in demineralized water and diluting to 100 ml. A boron stock solution containing 1 mg of boron per ml was prepared by dissolving 5.72 g of reagent grade boric acid in demineralized water and diluting to 1 l.

Standard nickel solutions containing 1.95, 1.63, 1.30, 0.65, and 0.33 mg of nickel per ml were prepared by making appropriate dilutions of the stock nickel solution. These solutions were prepared in aqueous form and also in 1 to 1 methanol–water.

Several sets of boron standard solutions were prepared, each set containing a fixed concentration of nickel as shown above, plus 0, 100, 200, 300, 400, and 500 μg of boron per ml. One set of boron solutions was made up containing no nickel and the same concentrations of boron as shown above. All solutions were prepared so that the final volume was a 1 to 1 methanol–water mixture.

A typical flame photometric standard solution containing 1.63 mg per ml nickel and 300 γ per ml boron would be prepared by pipetting out 250 μl of the nickel solution, 300 μl of the boron solution, adding 5 ml of reagent grade methanol and diluting to 10 ml. Demineralized water prepared by passing distilled water through Crystalab Deeminite ion exchange resin was used in the preparation of all solutions.

Flame spectrophotometer settings

The instrument settings for measuring the boron and nickel flame emission were as follows:

	Nickel	Boron
Sensitivity control, turns off clockwise limit	9	7
Selector switch	0.1	0.1
Phototube resistor, megohms	22	22
Slit, mm	0.1	0.1
Photomultiplier sensitivity control	3	3
Wave length, mμ	352.5	518
Oxygen pressure, lb./sq. in.	10	10
Hydrogen pressure, lb./sq. in.	3	3

Procedure

Pipet 250 μl of the sample solution into a 10 ml volumetric flask, add 5 ml of methanol, and dilute to volume with demineralized water. Measure the luminosity imparted to the flame at 352.5 mμ by the aspiration of this solution. Read the nickel content of the solution from the calibration curve shown in Fig. 1.

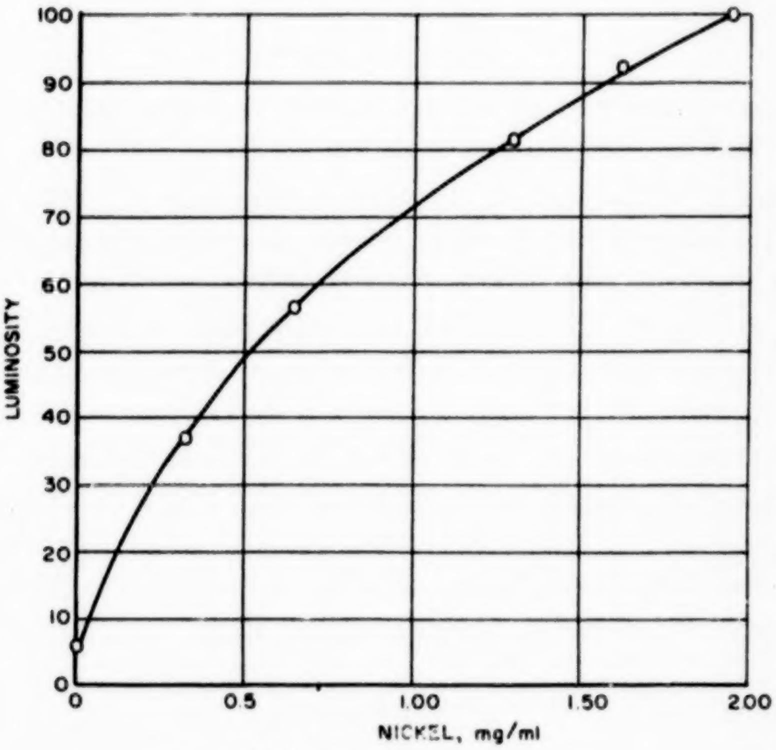

Fig. 1. Nickel calibration curve.

Change the settings of the spectrophotometer to the conditions for the boron determination as shown in the flame spectrophotometer settings and measure the luminosity of the flame at 518 mμ. This intensity represents the luminosity of the boron line superimposed upon the background contributed by the nickel emission. Determine the background luminosity imparted to the flame at 518 mμ by the nickel from the nickel background curve shown in Fig. 2. Subtract this background from the total luminosity of the flame at 518 mμ; this result is the boron contribution to the total luminosity measured. Use the boron calibration curve shown in Fig. 3 to determine the boron content of the aspirated solution.

Calculate the nickel and boron concentrations of the solution by applying the appropriate dilution factors to the results obtained above.

Effect of methanol on the flame emission of nickel

The intensity of the 352.5 mμ nickel line is increased greatly by the addition of methanol to the solution. This is illustrated in Fig. 4. The upper curve is a measure of the intensity when a 1 to 1 methanol–water mixture is used as the solvent for the nickel, while the lower curve is a measure of the intensity when water is used as the solvent. As is seen from the curve the difference in intensity increases with increasing

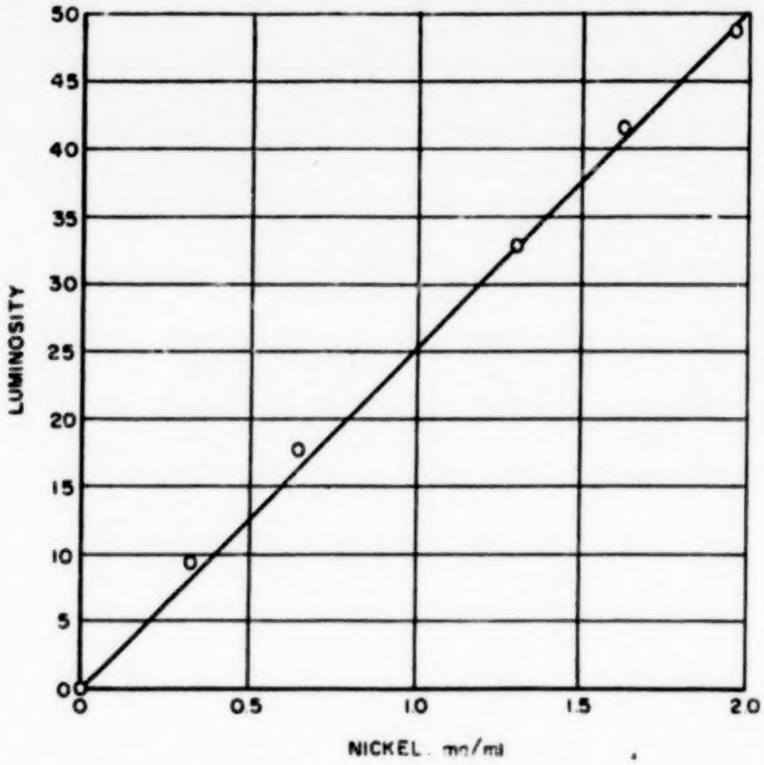

Fig. 2. Luminosity of nickel background at 518 mμ.

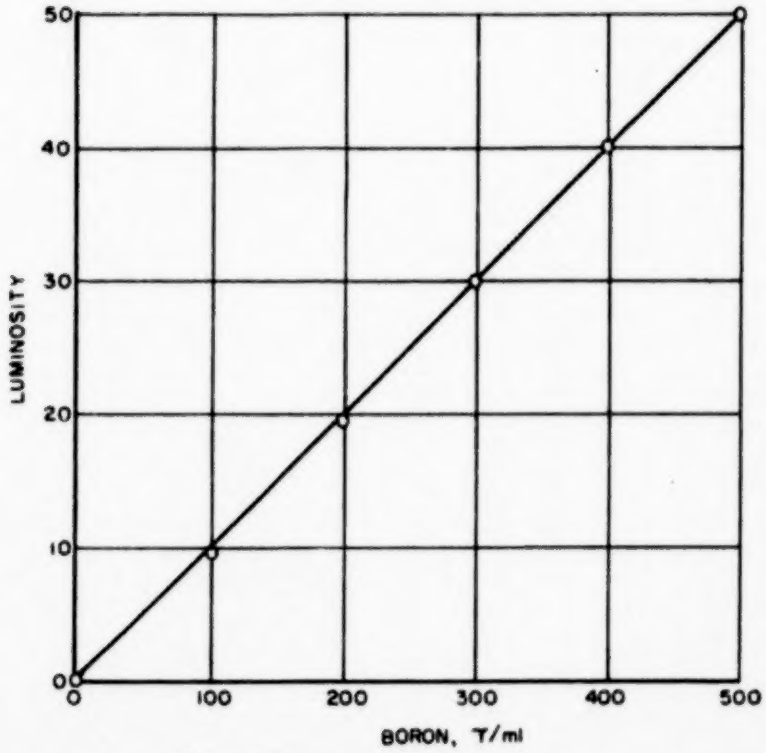

Fig. 3. Boron calibration curve.

nickel concentrations. This increase is not due to the interaction of the nickel with the methanol to form a more volatile nickel compound but is more likely related to the decrease in surface tension of the solution caused by the introduction of the methanol. Any decrease in the surface tension of the solution would cause a greater number of particles to be aspirated into the flame thereby increasing the probability of excitation and thus an increase in intensity of the flame emission.

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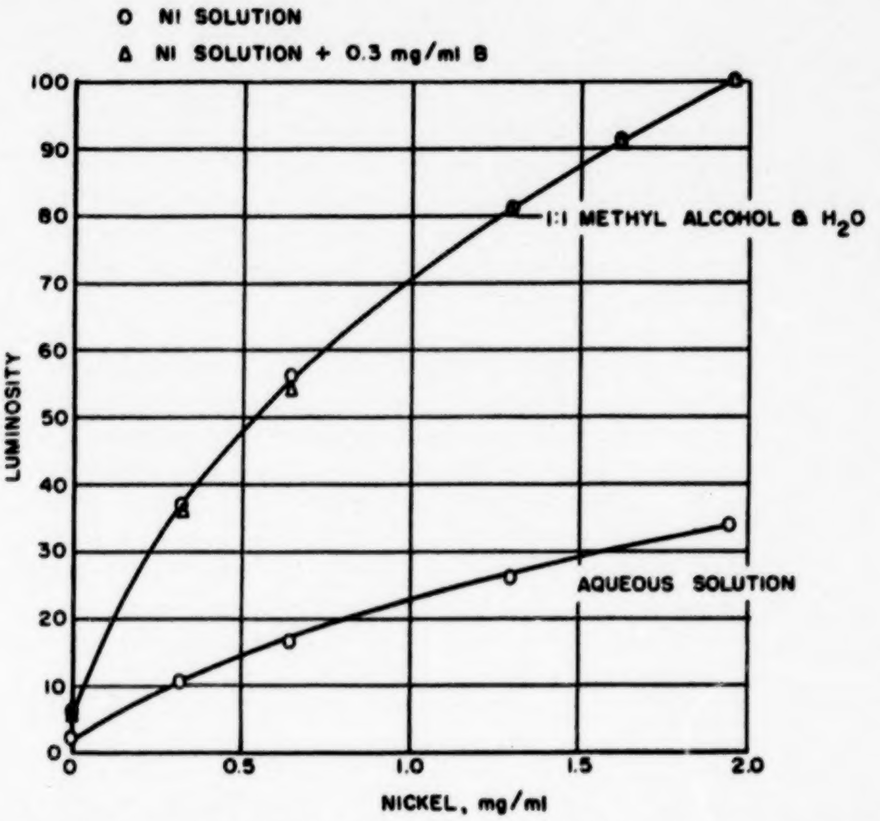

Fig. 4. Effect of methyl alcohol and boron on flame intensity of 352.5 mμ nickel line.

Interferences

Because all of the solutions used were prepared with the same reagents used in the plating solutions the effects of anion interferences were self compensating; therefore, no attempts were made to study them. As is shown in Fig. 4, the addition of 300 μg of boron per ml to a series of nickel solutions of varying concentrations had no effect on the luminosity of the 352.5 mμ nickel line.

The presence of nickel in the solutions had a pronounced additive effect upon the boron oxide emission band of 518 mμ. This enhancement is caused by a contribution to the flame background by the nickel. Fig. 2 shows that the intensity of the background flame emission at 518 mμ is a linear function of the nickel concentration.

Fig. 5 graphically illustrates the effect of adding nickel, at several concentration levels, to boron solutions of varying concentrations. It may be seen that for any point on the curve

$$L_{\mathrm{Ni\,+\,B}} - L_{\mathrm{Ni}} = L_{\mathrm{B}}$$

where: $L_{\mathrm{Ni\,+\,B}}$ = Luminosity of nickel-boron solution.
L_{Ni} = Luminosity of equal nickel concentration in absence of boron.
L_{B} = Luminosity of equal boron concentration in absence of nickel (see Fig. 3).

No attempts were made to study interferences of other metals since it was felt that the high concentrations of both boron and nickel would minimize their effects.

DISCUSSION OF RESULTS

Because of the lack of readily available standards, the results of the flame photometric determination were compared to those obtained by classical chemical methods

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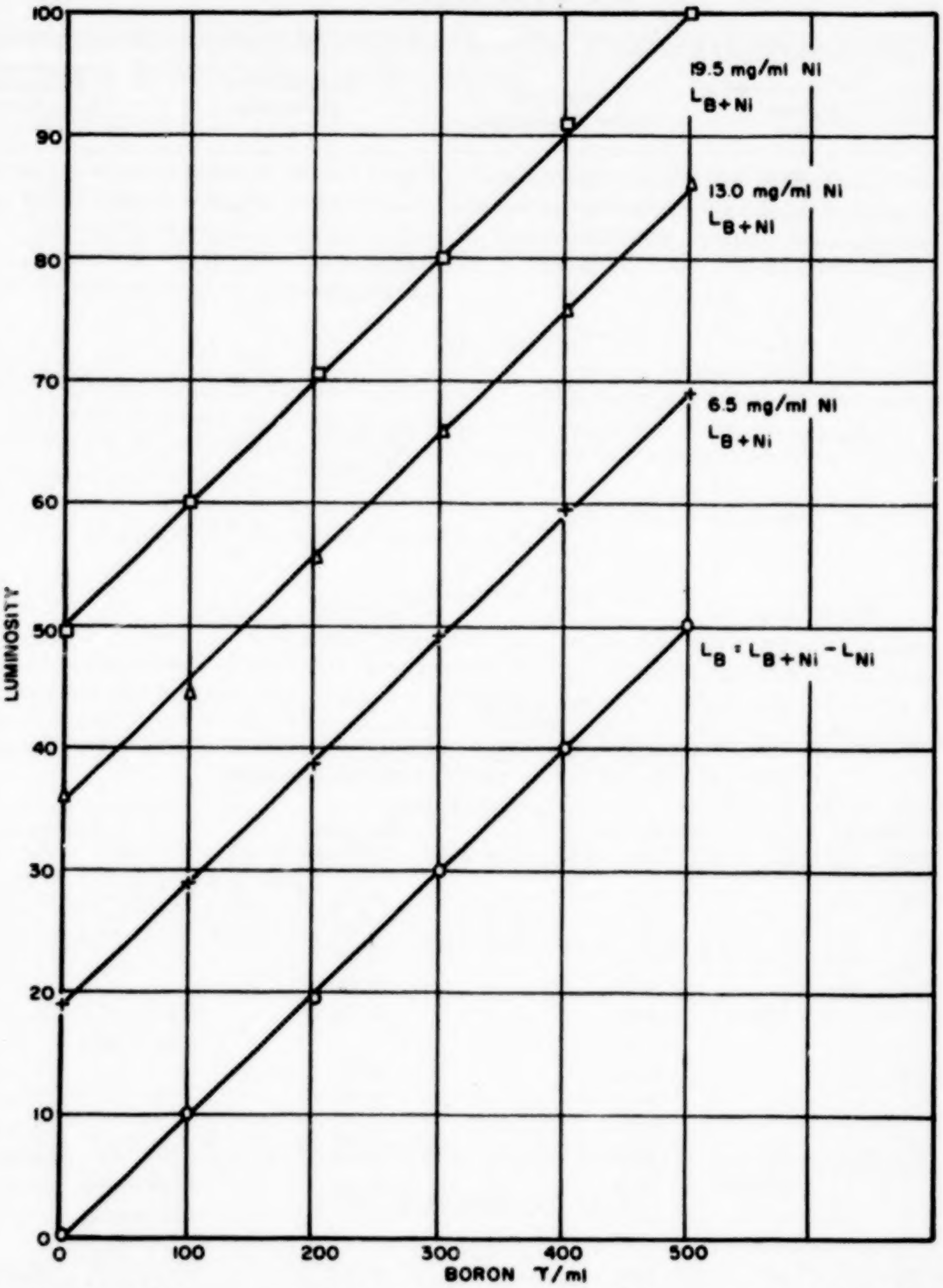

Fig. 5. Effect of nickel concentration on flame intensity of boron oxide band system at 518 mμ.

as shown in Table I. The flame photometric results agree quite well with the gravimetric results, both in precision and accuracy. The precision and accuracy of the flame photometric method are within 1%.

DEAN[2] has shown that the agreement between the flame photometric and volumetric boron determinations was within 1%; therefore, no efforts were made to compare the methods.

Table II shows the effect of varying nickel concentrations on the precision and accuracy of the flame spectrophotometric determination of boron. It can be seen that the nickel concentration of the solution has no appreciable effect on the precision and accuracy of the boron determination.

TABLE I

COMPARISON OF FLAME PHOTOMETRIC AND GRAVIMETRIC DETERMINATION OF NICKEL

Sample	*Nickel present mg*	*Nickel found gravimetric mg*	*Nickel found flame photometric*	*Relative error gravimetric %*	*Relative error flame photometric %*
1	32.5	30.0	32.5	−7.69	0
		33.8	32.5	+4.00	0
			32.5		0
		Mean 31.9	32.5	Error of the mean −1.85	0
2	16.3	16.0	16.3	−1.87	0
		16.3	16.4	0	+0.61
			16.3		0
		Mean 16.2	16.3	Error of the mean −0.61	0
3	6.5	6.3	6.5	−3.08	0
		6.5	6.5	0	0
			6.6		+1.54
		Mean 6.4	6.5	Error of the mean −1.54	0

TABLE II

EFFECT OF NICKEL CONCENTRATION ON PRECISION AND ACCURACY OF BORON DETERMINATION
(300 p.p.m. of boron present in all samples)

Sample	*Nickel present mg/ml*		*Boron found p.p.m.*	*Deviation %*		*Relative error %*
1	1.95		307	1.32		2.34
			297	0.99		1.00
			303	0.00		1.00
			305	0.66		1.67
		Mean	303	0.74	Error of the mean	1.00
2	1.30		295	1.67		1.67
			295	1.67		1.67
			310	3.33		3.33
			300	0.00		0.00
		Mean	300	1.67	Error of the mean	0.00
3	0.65		305	0.33		1.67
			303	0.33		1.00
			307	0.99		2.34
			298	1.98		0.67
		Mean	304	0.91	Error of the mean	1.33

CONCLUSIONS

The flame spectrophotometric method is a rapid and accurate means for the determination of nickel and boron in plating solutions. It is expected that the method described can be readily adapted to the determination of these elements in other solutions. The use of a methanol–water mixture as the solvent increases the flame intensity of both nickel and boron by a factor of about three. No attempts were made to determine the lower limits of detection; however, since there were two steps of photomultiplier sensitivity remaining, it is felt that the lower limit of detection for both nickel and boron will be less than 10 p.p.m.

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ACKNOWLEDGEMENT

The author gratefully acknowledges the laboratory assistance rendered by ELIZABETH S. HARRISON during the development of this method.

SUMMARY

The flame photometric method as a rapid means of estimating the nickel and boron concentrations in nickel plating solutions is described. The effect of methanol concentration upon the flame emission of the 352.5 mμ nickel line in 1 to 1 methanol – water solution was studied. The effect of nickel concentration upon the flame emission of boron in 1 to 1 methanol – water solution was studied for the oxide band system at 518 mμ.

RÉSUMÉ

On décrit la photométrie de flamme comme une méthode rapide d'estimation des concentrations de nickel et de bore dans les bains galvano-plastiques au nickel.

On étudie l'effet de la concentration du méthanol sur la flamme d'émission de la raie 352.5 mμ du nickel dans un mélange eau – méthanol 1 : 1.

L'effet de la concentration en nickel sur la flamme d'émission du bore dans un mélange eau – méthanol 1 : 1 est étudié pour les bandes de l'oxyde à 518 mμ.

ZUSAMMENFASSUNG

Die flammenphotometrische Methode wird als eine rasche Methode zur Bestimmung der Nickel- und Borkonzentrationen in Vernickelbädern beschrieben. Der Einfluss der Methanolkonzentration auf die Flammenemission der 352.5 mμ Nickellinie in einer 1 : 1 Methanol – Wasser-Lösung wurde untersucht. Der Einfluss der Nickelkonzentration auf die Flammenemission des Bors in 1 : 1 Methanol – Wasser-Lösung wurde für die Oxydbanden bei 518 mμ studiert.

REFERENCES

[1] N. H. FURMAN, *Scott's Standard Methods of Chemical Analysis*, Vol. 1, 5th Ed., D. Van Nostrand Co., Inc., New York, 1939, p. 614.

[2] J. A. DEAN AND C. THOMPSON, *Anal. Chem.*, 27 (1955) 42.

[3] H. WATANABE AND K. K. KENDALL, JR., *Appl. Spectroscopy*, 9 (1955) 132.

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THE WINKLER METHOD FOR DISSOLVED OXYGEN DETERMINATION

by

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Since its publication in 1888 the WINKLER method[1] of dissolved oxygen determination has undergone many modifications although the basic principle has remained unchanged. To a large extent these modifications, such as those due to ALSTERBERG[2] and to RIDEAL AND STEWART[3], are designed to avoid interference by oxidising or reducing compounds present in the water sample. More recently attention has been paid to extending the scope of the method and to making the final iodine estimation more accurate, particularly when the dissolved oxygen concentrations are low.

The accuracy at low dissolved oxygen values may be increased by extraction and concentration[4,5,6] before the final estimation of the iodine. This final estimation may be carried out photometrically as in the method of BAIRSTOW *et al.*[7], or of OVENSTON and Watson[6], colorimetrically as by Freier[8], or Wickert and Ipach[9], or amperometrically as by Knowles and Lowden[10]. The iodine has been determined also by direct potentiometric titration[11,12] employing conventional reference and indicator electrodes, or by a dead-stop end-point method[12].

This paper describes the use of a glass electrode as a reference electrode in the potentiometric titration of the iodine. The glass electrode has been used as a reference electrode in redox titrations[13,14,15,16], its use depending upon adequate acid buffering of the system to minimise any pH response of the electrode. The use of such an electrode largely eliminates liquid junction problems, introduces no extraneous ions into the solution, needs little maintenance in as much as solution replenishing is not required, and by choice of suitable electrode contents[13] the end-point potential may be varied. These features make the electrode assembly particularly attractive when automatic titration is required.

EXPERIMENTAL

The water sample was contained in a sample bottle of about 120 ml capacity and to it were added 1 ml of 48% w/v manganous sulphate and after mixing, 1 ml of potassium hydroxide-iodide solution (70% w/v potassium hydroxide, 15% w/v potassium iodide). The solution was well mixed and allowed to stand for 2 minutes when the resulting precipitate largely settled out. The bottle was then shaken and 1 ml of concentrated sulphuric acid added. Aliquots were placed in a beaker and titrated with standard sodium thiosulphate using a magnetic stirrer and a variable speed titration unit[16]. The electrode pair was a glass electrode and a platinum wire spiral, the potential being measured on a Pye pH – mV meter connected to a Honeywell-Brown strip chart recorder, the increased rate of change of potential at the end-point being used to switch off the titration unit[17,18].

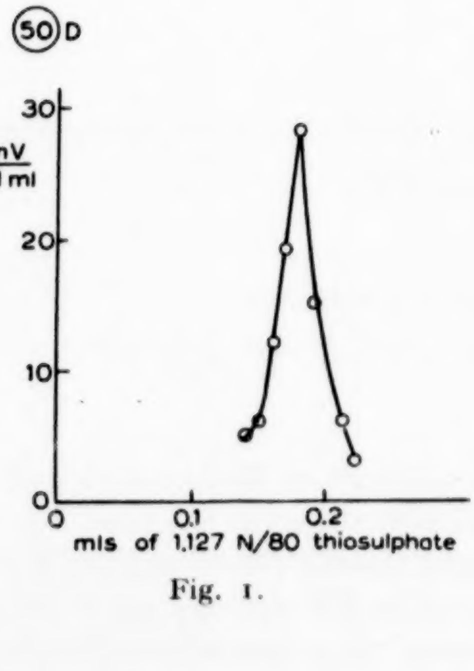

Fig. 1.

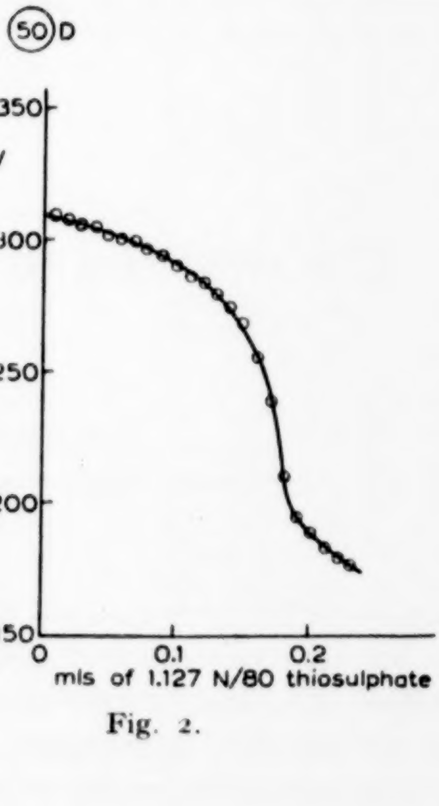

Fig. 2.

RESULTS

A typical experimental curve is shown in Figs. 1 and 2. The rate of change of potential at the end-point using $N/80$ sodium thiosulphate solution is of the order of 2,400 mV/ml.

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A number of lithium glass electrodes was used and the end-point potential appears sensibly independent of the electrode used. The reproducibility of this potential was good over the dissolved oxygen range studied (0.4–4.4 p.p.m.) and had an average value of 211 mV.

Titration 50 D

A 50 ml aliquot of the sample was titrated using 1.127 $N/80$ sodium thiosulphate. End-point = 0.18 ml of sodium thiosulphate; hence, the dissolved oxygen concentration in original sample $= \dfrac{0.18 \times 1.127 \times 10^2 \text{ p.p.m.}}{50} = 0.406$ p.p.m.

SUMMARY

A modification of the Winkler method of dissolved oxygen determination is described in which the final iodine titration is carried out potentiometrically using a glass and a platinum electrode as reference and indicator respectively.

The method has been made automatic and the apparatus used has the advantage of considerable flexibility in operation.

Since the reproducibility of end-point potential is good, an alternative method of concluding the titration becomes available. This involves switching off the titration unit when the potential of the end-point is reached, by means of a circuit such as that of AUDRAN AND DIGHTON[19] or, more simply, by a method developed by one of the authors (M.I.J.) using a recorder or millivoltmeter and a photo-transistor operated relay.

RÉSUMÉ

On propose une modification à la méthode de Winkler pour le dosage de l'oxygène dissous. La titration volumétrique par le thiosulfate de sodium est remplacée par une titration potentiométrique. L'électrode de référence utilisée est en verre, tandis que l'indicateur est une électrode de platine.

ZUSAMMENFASSUNG

Eine Modifikation der Winkler'schen Methode zur Bestimmung von gelöstem Sauerstoff wird vorgeschlagen. Hierbei wird die volumetrische Natriumthiosulfat-Titration durch eine potentiometrische Titration ersetzt. Die Vergleichselektrode ist aus Glas, während als Indikator eine Platinelektrode dient.

REFERENCES

[1] L. W. WINKLER, *Ber.*, 21 (1888) 2843.
[2] G. ALSTERBERG, *Biochem. Z.*, 159 (1925) 36.
[3] S. RIDEAL AND G. STEWART, *Analyst*, 26 (1901) 141.
[4] J. ARNOTT AND J. MCPHEAT, *Engineering*, 176 (1953) 103.
[5] J. ARNOTT AND J. MCPHEAT, *Engineering*, 169 (1950) 553.
[6] T. C. J. OVENSTON AND J. H. E. WATSON, *Analyst*, 79 (1954) 383.
[7] S. BAIRSTOW, J. FRANCIS AND G. H. WYATT, *Analyst*, 72 (1947) 341.
[8] R. FREIER, *Vom Wasser*, 19 (1952) 124.
[9] K. WICKERT AND E. IPACH, *Z. anal. Chem.*, 140 (1953) 350.
[10] G. KNOWLES AND G. F. LOWDEN, *Analyst*, 78 (1953) 159.
[11] A. S. T. M. Standards, (1949) D. 888 - 49T.
[12] British Standards, 2690 (1956) 87.
[13] V. S. GRIFFITHS AND D. I. STOCK, *J. Chem. Soc.*, (1956) 1633.
[14] L. LYKKEN AND F. D. TUEMMLER, *Ind. Eng. Chem., Anal. Ed.*, 14 (1942) 67.
[15] F. L. WYND, *Ann. Missouri Botan. Garden*, 22 (1935) 361.
[16] V. S. GRIFFITHS AND M. I. JACKMAN, in course of publication.
[17] H. V. MALMSTADT AND E. R. FETT, *Anal. Chem.*, 26 (1954) 1348.
[18] H. V. MALMSTADT AND E. R. FETT, *Anal. Chem.*, 27 (1955) 1757.
[19] R. AUDRAN AND D. J. DIGHTON, *J. Sci. Instr.*, 33 (1956) 92.

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Short Communications

A note on the paper electrophoretic separation of inorganic anions

Relatively few separations of inorganic anions have so far been recorded by paper electrophoresis. Most efforts were centred on phosphorus acids[1] and sulphur acids[2]. Only *N* KCl was investigated for several of the usual anions[3].

Recently SCHIER[4] has separated the alkali metals using a solution of ammonium carbonate as electrolyte. This electrolyte appeared to us to have the qualifications necessary for the paper electrophoresis of most anions: sufficient alkalinity to prevent decomposition (*e.g.* for sulphites, halogen oxyacids, nitrites etc.), an electrolytic strength of a strong electrolyte combined with a high volatility at rather low temperatures, the latter permitting detection with indicators as well as with acid sprays after a few minutes drying in an oven.

As apparatus we used the large model moist chamber constructed by Jouan et Cie. The paper (Arches No. 302) was dipped into a 2% ammonium carbonate solution dried between blotting paper and clamped into the apparatus which contained 400 ml of 2% ammonium carbonate in each electrode compartment. Microspots of the anions or anion mixtures were applied on a line 1.5 cm from the border of the cathode compartment and the potential of 150 V applied for one hour. The liquid flow due to evaporation and lack of saturation of the paper was quite considerable in these experiments. We tried to test its order of magnitude as shown by DE WAEL[5] by placing spots of CrO_4^{-2} and of H_2O_2 at various distances from the cathode department. As shown in Fig. 1 the decrease of movement is linear.

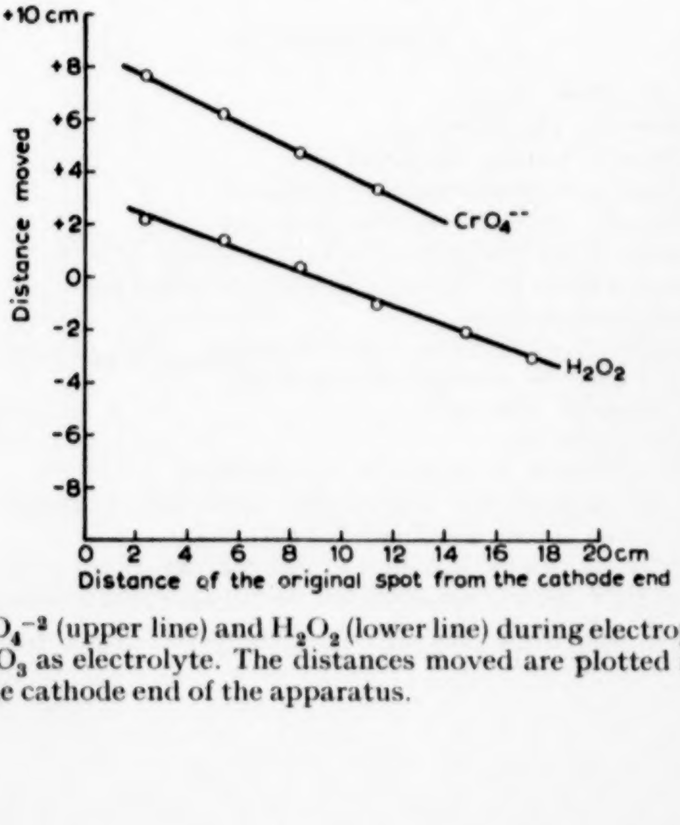

Fig. 1. Movement of CrO_4^{-2} (upper line) and H_2O_2 (lower line) during electrophoresis for 1 hour with 150 V and 2% $(NH_4)_2CO_3$ as electrolyte. The distances moved are plotted against the distance of the original spot from the cathode end of the apparatus.

Table I shows the movement of anions when placed at 1.5 cm from the cathode. The apparatus permits the simultaneous running of eight samples. In order to get comparable values from sheet to sheet (to correct for temperature and saturation differences) we placed CrO_4^{-2} on all sheets. Its movement was 75, 78, 73, 76, 74, 74, 73, 71 mm on the paper sheets on which all other anions were electrophorised. The movement of anions in Table I was thus corrected to the equivalent of a CrO_4^{-2} movement of 75 mm.

It was found remarkable that under alkaline conditions there is little difference in the movement of mono-, di- and trivalent anions such as Cl^-, sulphate and ferricyanide.

TABLE I

THE MOVEMENT OF INORGANIC ANIONS DURING PAPER ELECTROPHORESIS FOR 1 HOUR WITH 150 V AND 2% AMMONIUM CARBONATE AS ELECTROLYTE IN THE JOUAN MOIST CHAMBER APPARATUS

The movement is expressed in mm and differences from sheet to sheet adjusted for by correcting to the distance moved by CrO_4^{-2} = 75 mm.

Anion	*mm*	*Anion*	*mm*
Borate	33	Fluoride	67
Arsenite	36.5	Thiocyanate	64
Arsenate	61	Sulphite	70
Phosphate	59	Thiosulphate	86
Pyrophosphate	57	Sulphate	78
Graham's salt	56	Persulphate	80
Nitrite	83	Selenite	60
Nitrate	83	Tellurite	49
Chloride	80	Tellurate	38 with comet
Chlorate	76	Pertechnetate	59
Bromide	83	Perrhenate	59
Bromate	67	Ferrocyanide	85
Iodide	82	Ferricyanide	72
Iodate	50	Metavanadate	60
Periodate	two spots at 0 and 11 mm also a reduction comet	Molybdate	**61**
		Uranylcarbonate	63

There are several useful separations, which have not been previously observed, in the region of the halogen oxyacids. Mixtures of ClO_3^-, BrO_3^- and IO_3^- could be separated; also mixtures of BrO_3^-, IO_3^- and IO_4^-. However, periodate is partially reduced as well as divided into two distinct spots which move very little.

Other interesting separations are that of borate from numerous anions and the separations arsenite-arsenate and selenite-tellurite which have been carried out before in other electrolytes.

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[1] B. SANSONI AND R. KLEMENT, *Angew. Chem.*, 65 (1953) 422; 66 (1954) 598.
[2] H. W. WOOD, *Nature*, 175 (1955) 1084; *Chem. & Ind.* (*London*), (1956) 468.
[3] M. LEDERER AND F. L. WARD, *Anal. Chim. Acta*, 6 (1952) 355.
[4] O. SCHIER, *Angew. Chem.*, 68 (1956) 63.
[5] J. DE WAEL, *Chem. Weekblad*, 49 (1953) 229; *Ciba Symposium on Paper Electrophoresis, July 1955*, J. & A. Churchill Ltd, London, publ. 1956.

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Die Bestimmung von Schwefelverbindungen nebeneinander mit Ferricyanid unter Verwendung von Osmiumtetroxyd als Katalysator

Es ist bekannt, dass die oxydimetrische Bestimmung gewisser anorganischer Schwefelverbindungen (Sulfid, Sulfit, Dithionit, Tetrathionat, usw.) in saurem Medium wegen der Luftoxydation dieser Verbindungen sowie wegen der oft nicht eindeutigen Reaktionen auf Schwierigkeiten stösst. Genauere Ergebnisse lassen sich erzielen, wenn die Oxydation mit Hilfe von geeigneten Messlösungen (z.B. mit Natriumhypobromitlösung) in alkalischem Medium vorgenommen wird. Aber auch unter Zuhilfenahme dieser Messlösungen ist die Bestimmung von Schwefelverbindungen nebeneinander nur nach komplizierten Abtrennungsverfahren zu verwirklichen.

Anlässlich der Untersuchung der Oxydationsreaktionen des Ferricyanids konnten wir unlängst feststellen*, dass das Osmiumtetroxyd einen allgemeinen Katalysator für die Oxydationsreaktionen des Ferricyanids darstellt. Mit Hilfe dieser Katalyse haben wir Methoden zur schnellen Bestimmung verschiedener Schwefelverbindungen ausgearbeitet.

1. Nach unseren Untersuchungen können Sulfit, Bisulfit, Pyrosulfit, Sulfid, Dithionit, Thiosulfat und Tetrathionat (nach Disproportionierung in Sulfit und Thiosulfat) in einem Medium von 4-5*N* Natriumhydroxyd in Gegenwart von Osmiumtetroxyd bei 50-60°C mit Ferricyanid augenblicklich quantitativ zu Sulfat oxydiert werden. Bei schnellen Titrierungen stört der Luftsauerstoff nur bei der Dithionit- und Tetrathionat-Messung, was aber durch Schaffung einer N_2-Atmosphäre leicht zu vermeiden ist. Der Endpunkt der Messungen kann mittels Dead-stop- oder potentiometrischer Methode ermittelt werden.

2. In Anbetracht dessen, dass das Dithionit bei Laugenkonzentrationen von 0.2-1*N* bei Zimmertemperatur mit Ferricyanid nur bis zum Sulfit oxydierbar ist und diese Titration durch die Anwesenheit grösserer Mengen Thiosulfat, Rhodanid und Sulfit gar nicht gestört wird, gelang es, eine Methode zur Bestimmung von Dithionit-Sulfit und Dithionit-Thiosulfat nebeneinander auszuarbeiten. Dementsprechend wird das Dithionit in schwach alkalischer Lösung zu Sulfit oxydiert, sodann die Laugenkonzentration auf 4-4.5*N* erhöht, und unter Zusatz von einigen Tropfen Osmiumtetroxyd wird die Bestimmung des bei der Dithionitmessung entstehenden Sulfits und der anderen anwesenden Schwefelverbindung mit Ferricyanid vorgenommen.

3. Mit Jod als Hilfsreagens kann auch die sukzessive Bestimmung von Sulfit-Thiosulfat, Tetrathionat-Thiosulfat und Dithionit-Sulfit-Thiosulfat durchgeführt werden. So lässt sich z.B. die Bestimmung von Dithionit, Sulfit und Thiosulfat nebeneinander folgendermassen verwirklichen. In der ersten Probe wird bei 1*N* Laugenkonzentration und Zimmertemperatur das Dithionit bestimmt. Nach der Titration wird die Laugen-

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* F. Solymosi, *Naturwiss.*, 44 (1957) 374.

konzentration auf 4-4.5N erhöht und unter Verwendung von Osmiumtetroxyd bei 50-60°C anwesende Sulfit- und Thiosulfat-Ionen mit Ferricyanid zu Sulfat oxydiert. Eine zweite Probe wird mit Jod behandelt, worauf aus Dithionit und Sulfit Sulfat, und aus dem Thiosulfat Tetrathionat gebildet wird, welche ähnlich wie vorher angegeben, in Gegenwart von Osmiumtetroxyd mit Ferricyanid bestimmt werden. In Kenntnis der drei Ferricyanidtitrationen kann auf Grund einfacher Berechnungen die Menge der einzelnen Schwefelverbindungen angegeben werden. Auf Grund des gleichen Prinzips können auch die übrigen Nebeneinander-Bestimmungen durchgeführt werden.

Über weitere eingehende Untersuchungen soll demnächst berichtet werden.

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A. Varga

Eingegangen den 28. August 1957

REVUE DE LIVRE

The Principles and Applications of Polarography and other Electroanalytical Processes, par G. W. C. Milner, Atomic Energy Research Establishment, Harwell, Longmans, Green and Co., London, 1957, 729 pages, Prix 90/–.

Monsieur G. W. C. Milner, spécialiste des méthodes électrochimiques d'analyse vient de publier un livre sur la polarographie et sur les disciplines qui s'y rattachent. C'est donc un vaste domaine qu'il embrasse. Aussi, ne peut-on reprocher à l'auteur de n'avoir donné qu'une bibliographie partielle.

Ce livre comprend 4 parties: Théorie, appareillage et technique, polarographie inorganique, polarographie organique et titrage ampérométrique.

Les bases théoriques de la polarographie: courant de diffusion — courbes potentiel-courant — électrode à goutte etc. font l'objet de la première partie. Elles sont exposées avec clarté et de façon approfondie. On y trouve aussi une description de l'appareillage et de l'équipement. Un chapitre est consacré aux développements modernes tels que la polarographie oscillographique et différentielle et la polarographie en milieu non aqueux. Cette partie se termine par l'électrolyse à potentiel constant et ses applications à la polarographie et à l'analyse coulométrique.

La seconde partie traite de la polarographie inorganique. On y trouve dans l'ordre alphabétique chaque élément avec ses propriétés essentielles et quelques exemples de dosages.

La troisième partie a pour objet les substances organiques et biologiques et la dernière a trait au titrage ampérométrique, soit avec l'électrode à goutte de mercure, soit avec l'électrode de platine tournante.

Ce livre important est fort bien présenté, l'exposé y est clair, la partie théorique est particulièrement soignée et détaillée et comprend les conceptions les plus modernes. Nous nous faisons un plaisir de le recommander aux lecteurs de cette revue.

D. Monnier (Genève)

SOME RECENTLY PUBLISHED BOOKS

R. Adams, *Organic Reactions*, Vol. IX, John Wiley & Sons, Inc., New York, 1957, 470 pages, $ 12.00.

W. Bahrdt und R. Scheer, *Stöchiometrische Aufgabensammlung*, Walter de Gruyter & Co, Berlin, 1957, 118 pages, DM 2.40.

R. W. Cowgill and A. B. Pardee, *Experiments in Biochemical Research Techniques*, John Wiley & Sons, Inc., New York, 1957, 189 pages, $ 3.50.

E. J. Crane, A. M. Patterson and E. B. Marr, *A Guide to the Literature of Chemistry*, John Wiley & Sons, Inc., New York, 1957, 2nd edition, 397 pages, $ 9.50.

F. R. Eirich, *Rheology: Theory and Applications*, Academic Press Inc., New York, Vol. I, 1956, 761 pages, $ 20.—, Vol. II, 1957, ∼ 500 pages, Vol. III, ∼ 450 pages.

R. C. Elderfield, *Heterocyclic Compounds*, Vol. 6, Six-Membered Heterocycles Containing Two Hetero Atoms and Their Benzo Derivatives, John Wiley & Sons, Inc., New York, 1957, 753 pages, $ 25.—.

S. W. Fox and J. F. Foster, *Introduction to Protein Chemistry*, John Wiley & Sons, Inc., New York, 1957, 459 pages, $ 9.50.

G. L. Jenkins, W. H. Hartung, K. E. Hamlin Jr. and J. B. Data, *The Chemistry of Organic Medicinal Products*, John Wiley & Sons, Inc., New York, 1957, 569 pages, $ 10.75.

W. Kauzmann, *Quantum Chemistry*, Academic Press Inc., New York, 1957, ∼ 760 pages, approx. $ 13.—.

G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, Inc., New York, 1957, 269 pages, $ 6.75.

E. G. Rochow, D. T. Hurd and R. N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley & Sons, Inc., New York, 1957, 344 pages, $ 8.50.

K. Schmeiser, *Radioaktive isotope, ihre Herstellung und Anwendung*, Springer-Verlag, Berlin, 1957, XI, 246 pages, DM 48.60.

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